

General Adhesion: Methods of Contact Mechanics

Manoj K. Chaudhury
Dept. of Chemical Eng
Center for Polymer Interfaces
Lehigh University

Outline

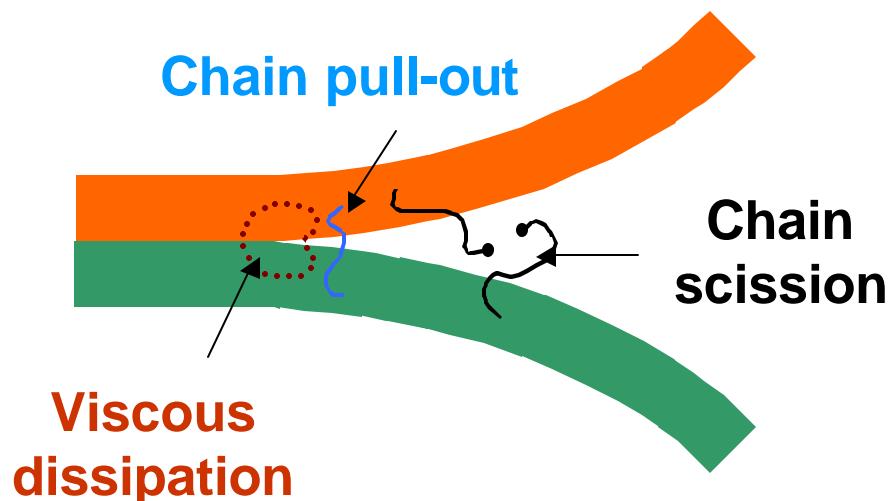
- Introduction to JKR Contact Mechanics
- Estimation of the Surface and Adhesion Energy of Solids
- Other Contact Mechanics Methods
- Peel, Adhesion, Interfacial Instability

Adhesion



- Van der Waals interaction
- Inter-diffusion
- Entanglement of polymer chains
- Covalent bonding

Fracture



- Bond breaking kinetics
- Chain pull-out
- Viscous dissipation

Strength of an adhesive joint

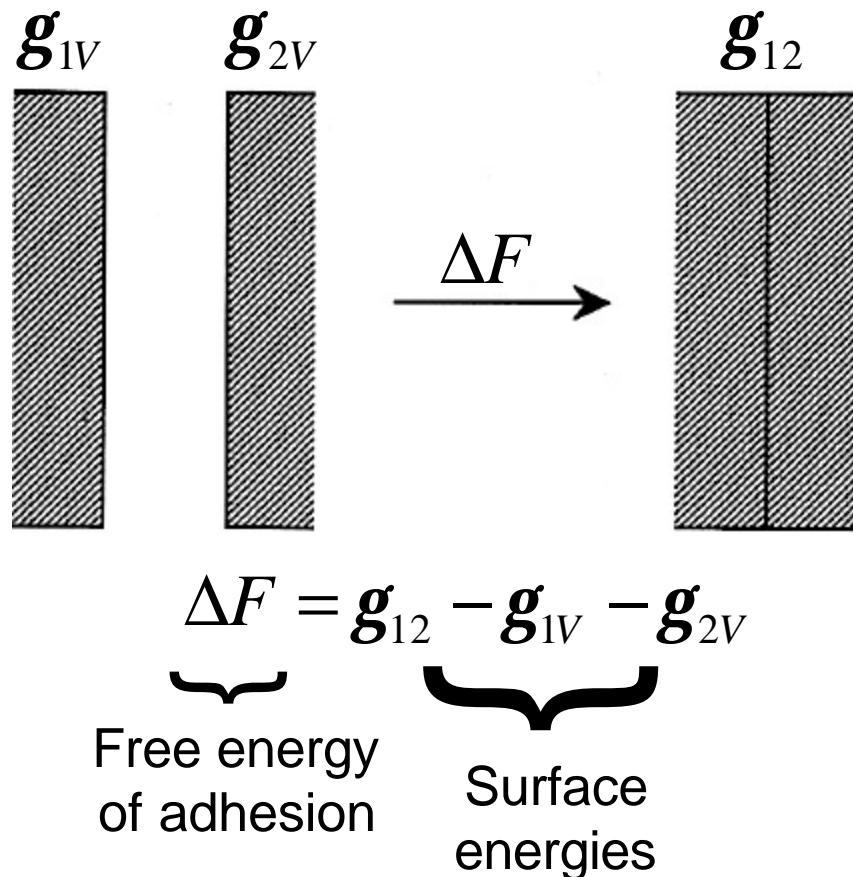


$$\text{Strength of a joint} = \text{Strength of interface} \times \text{Viscoelastic amplification}$$

**Understanding interface is
a good starting point**

Understanding Interfacial Adhesion

Thermodynamics:



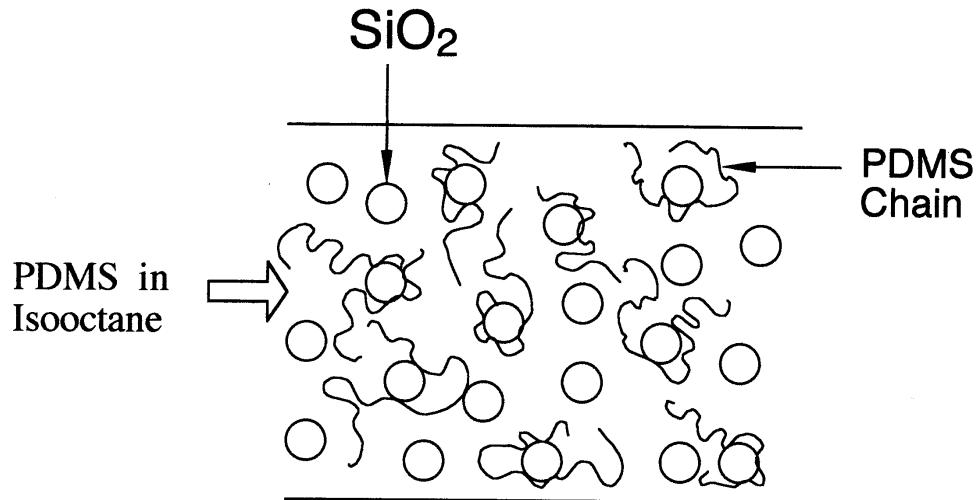
Structure-property relationship:

Prediction based on

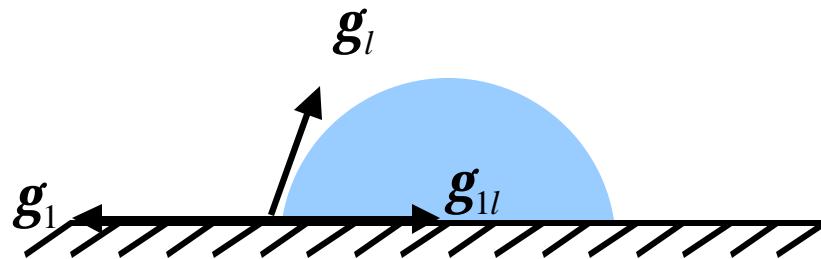
Orientation
Polarity
Polarizability
Donor-Acceptor interaction

Thermodynamic methods to estimate energy of interaction

Heat of Adsorption:



Wettability:



$$g_l(1 + \cos q) = g_1 - g_{1l}$$

Good, Girifalco
and Fowkes Eq.

$$\downarrow$$

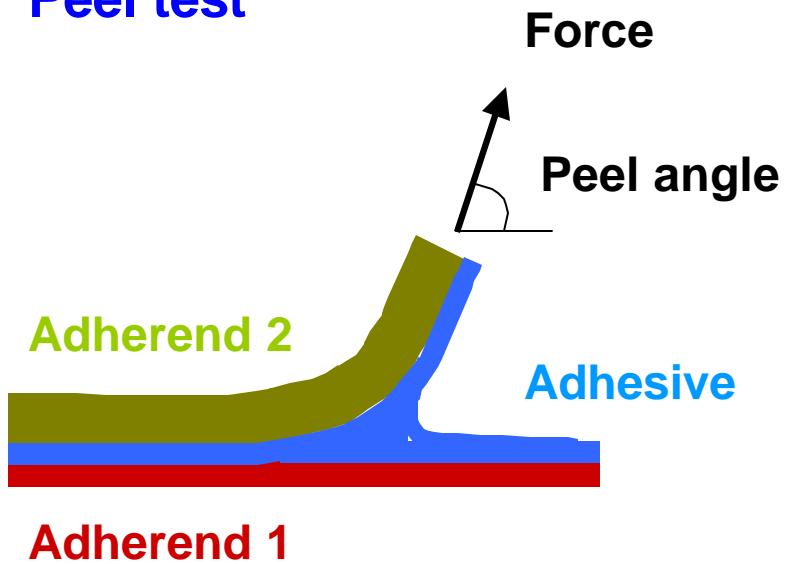
$$g_1$$

$$\downarrow$$

$$\Delta F_{12}$$

Various methods used to estimate fracture energy

Peel test



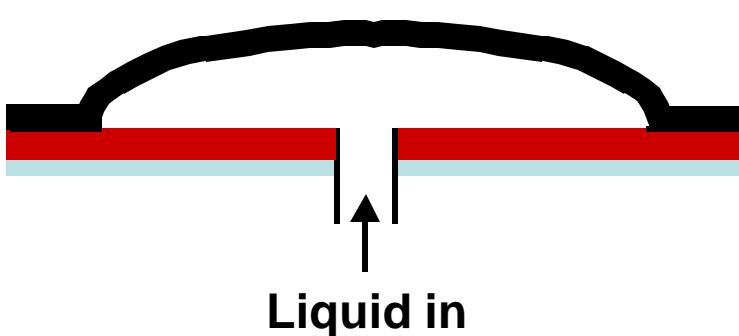
Single overlap shear test



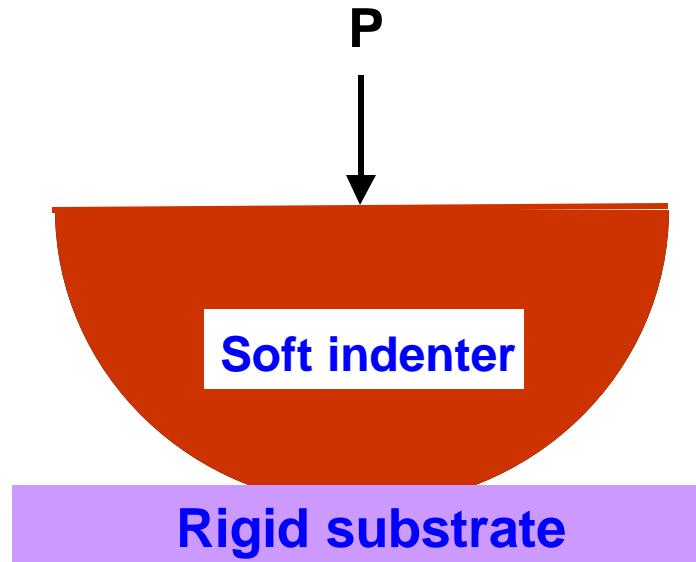
Double overlap shear test



Blister test



A direct method to estimate adhesion and surface energy

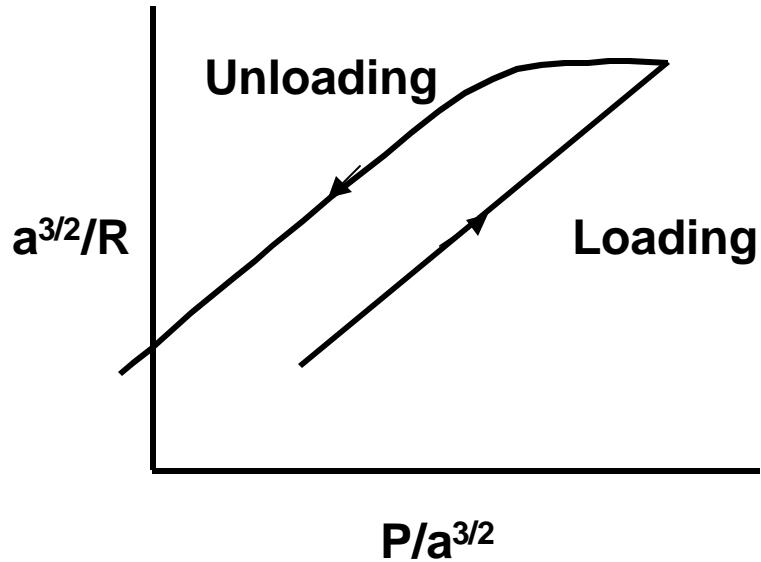


$$W = \frac{\left(P - \frac{4Ea^3}{3R} \right)^2}{8pEa^3}$$

Rearranging,

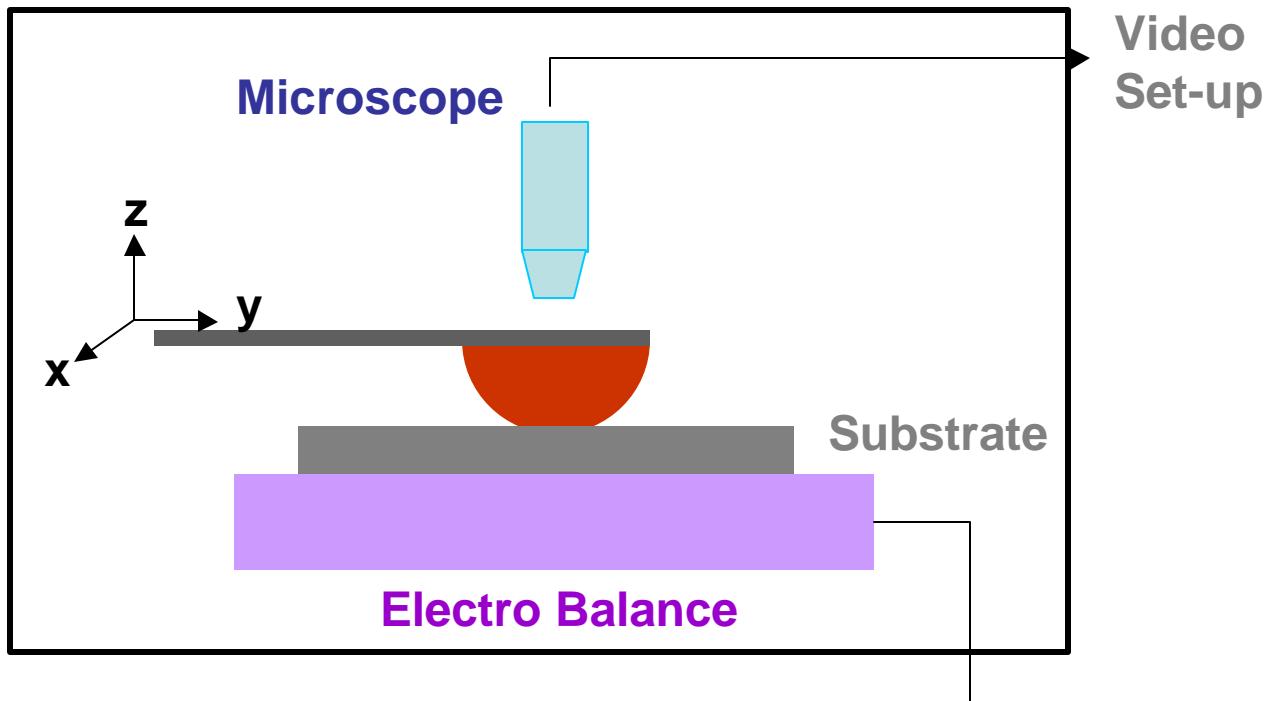
$$\frac{a^{1.5}}{R} = \frac{9}{16E} \frac{P}{a^{1.5}} + \frac{3}{4} \left(\frac{6pW}{E} \right)^{0.5}$$

Adhesion Hysteresis



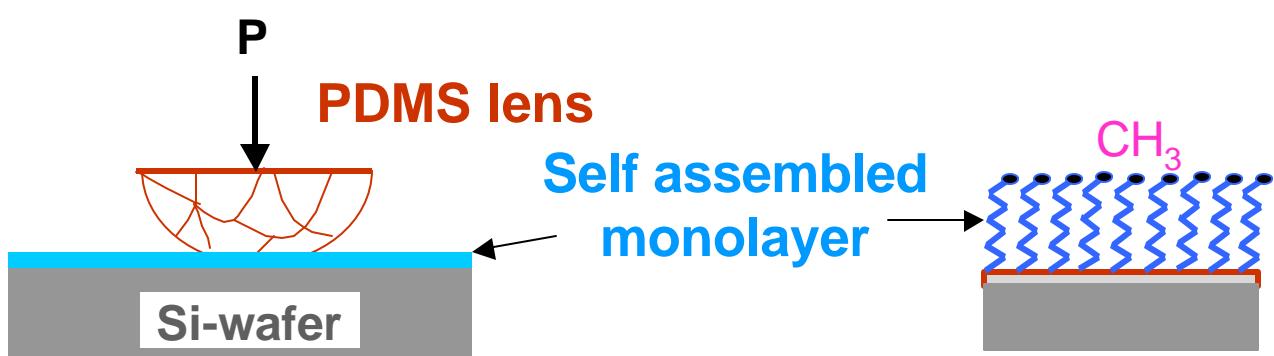
- Viscoelastic
- Interfacial

Controlled environment

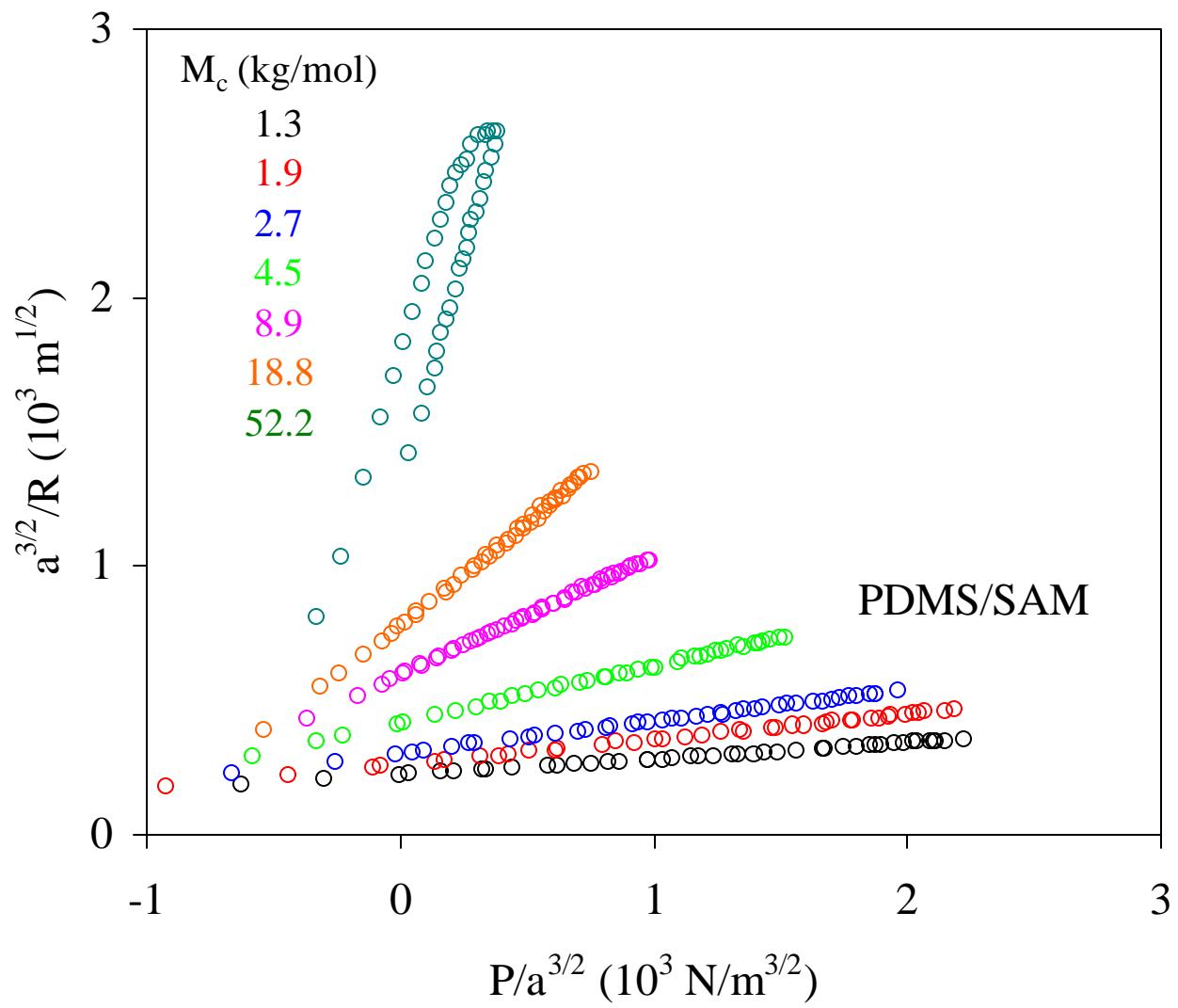


Example

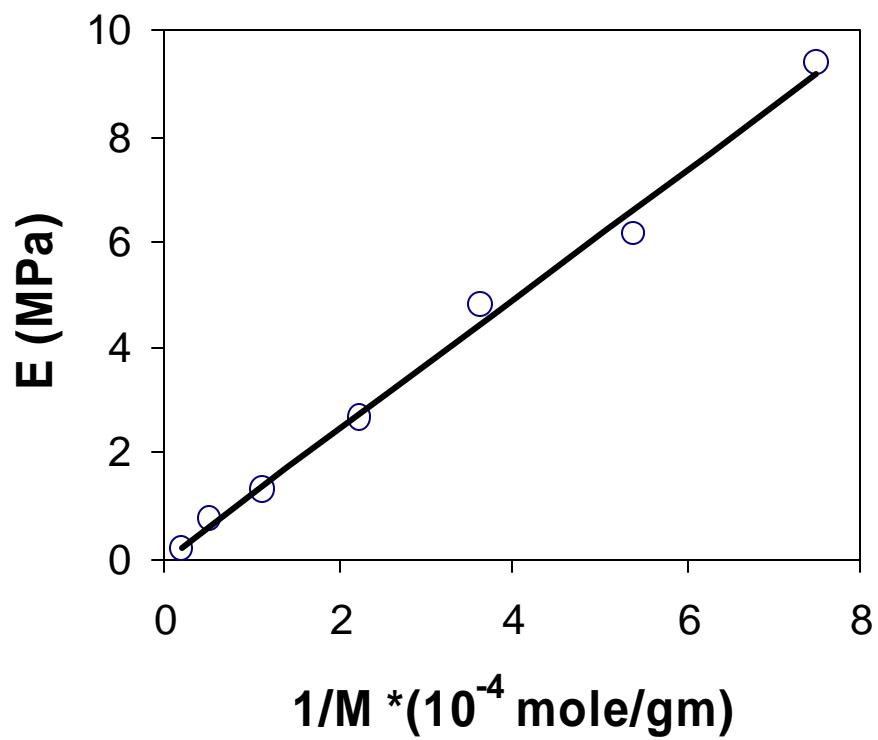
Computer



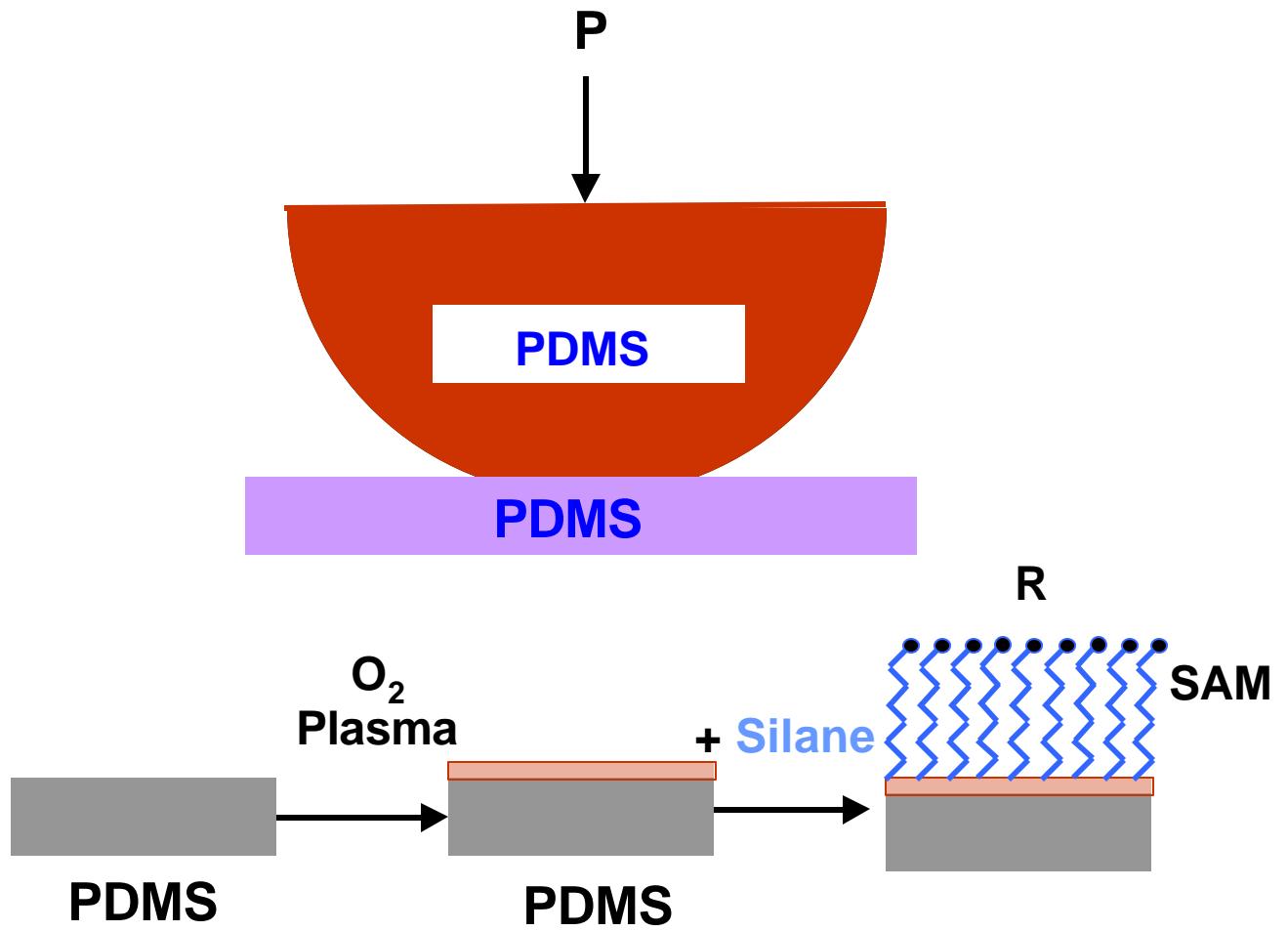
PDMS of MW 1 K – 50 K



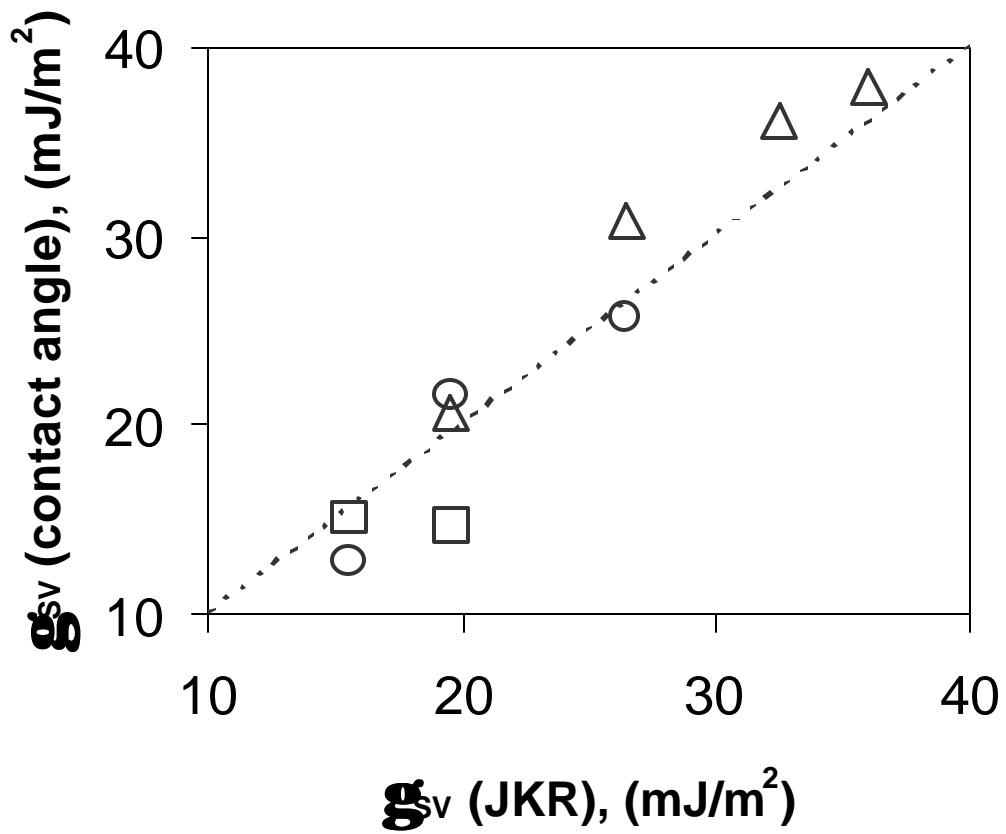
M (g/mol)	W advancing (mJ/m ²)	W receding (mJ/m ²)
1.3K	42.4	45.1
1.9	41.3	41.8
2.7	44.1	45.8
4.5	43.0	43.6
8.9	42.7	43.2
18.8	41.4	42.6
52.2	27.0	55.9



Deformable elastomer of various surface energies

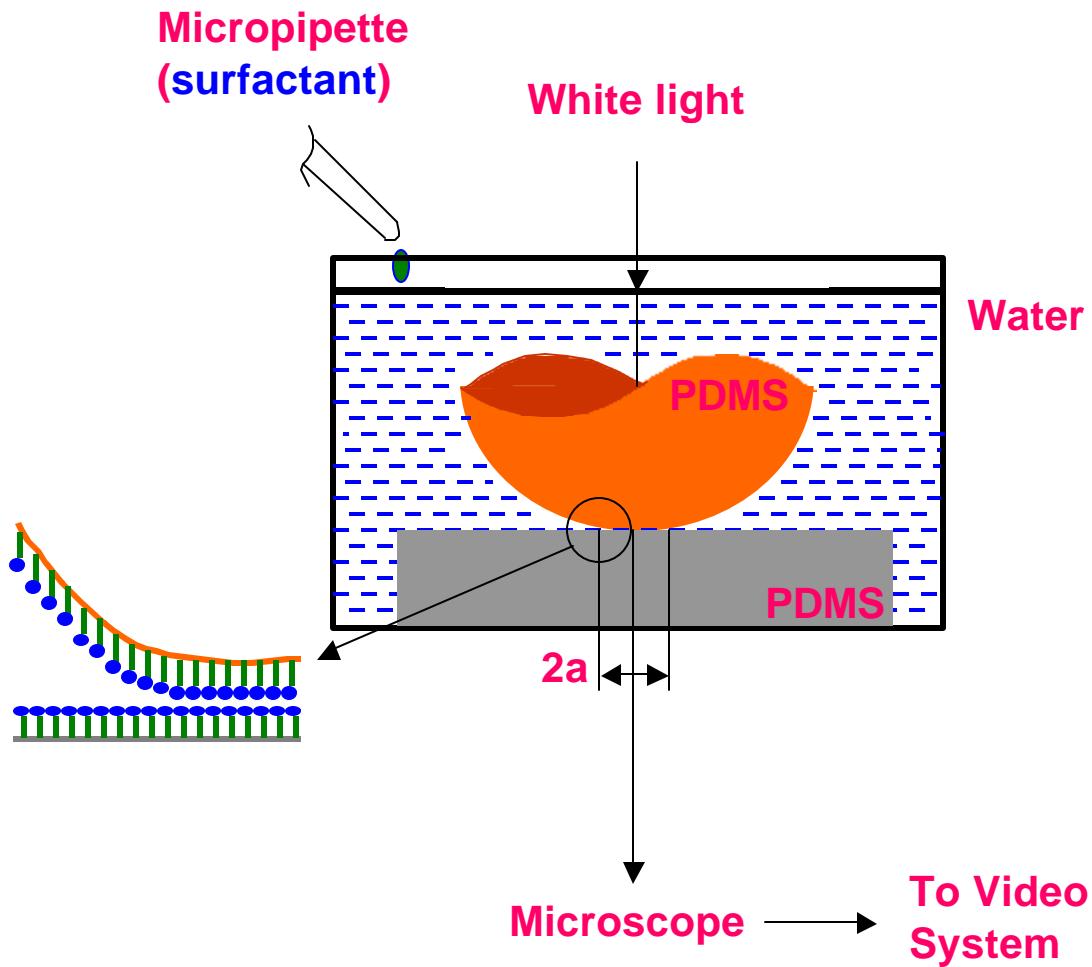


$R = \text{CH}_3, \text{CF}_3, \text{CH}_2\text{Br}, \text{CH}_2\text{OH}, \text{CO}_2\text{H}, \text{NH}_2, \text{etc.}$

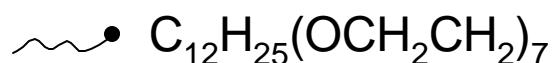


$R = \text{CH}_3, \text{CF}_3, \text{CH}_2\text{Br}, \text{CO}_2\text{CH}_3,, \text{OCH}_3$

JKR measurements can be done under a liquid

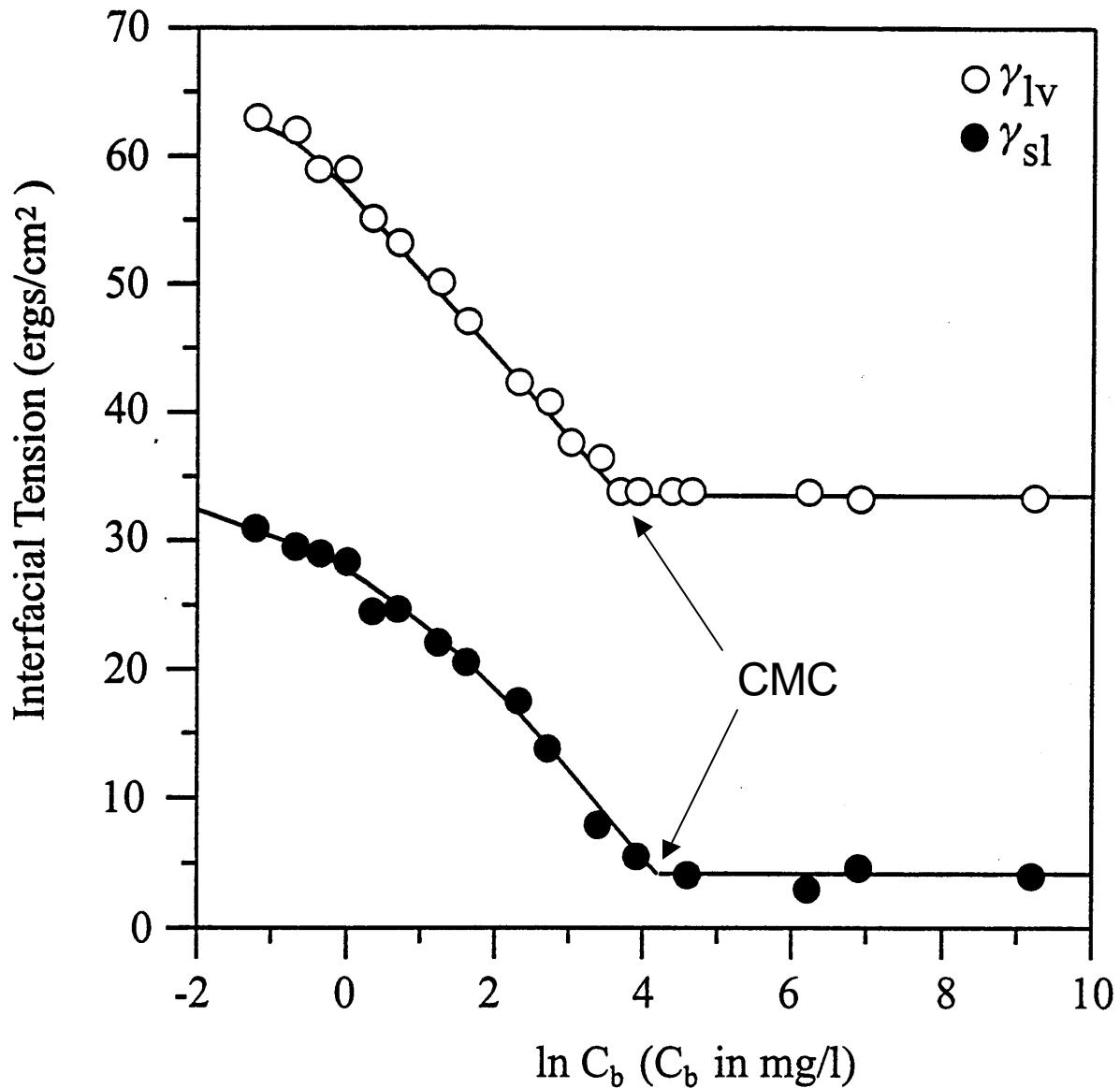


Structure of a surfactant



Haidara, Chaudhury, Owen

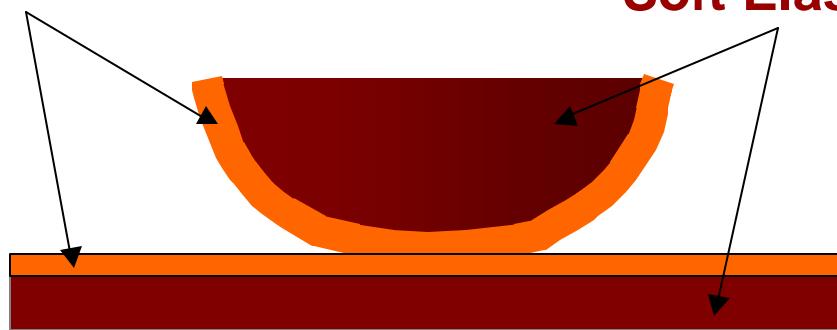
Gibbs Plots for liquid-vapor and liquid-solid interfaces



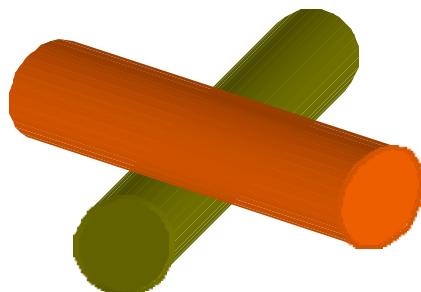


**Mica coated
with polymers**

Polymer films



Soft Elastomers



**Cross cylinders
coated with
polymers**

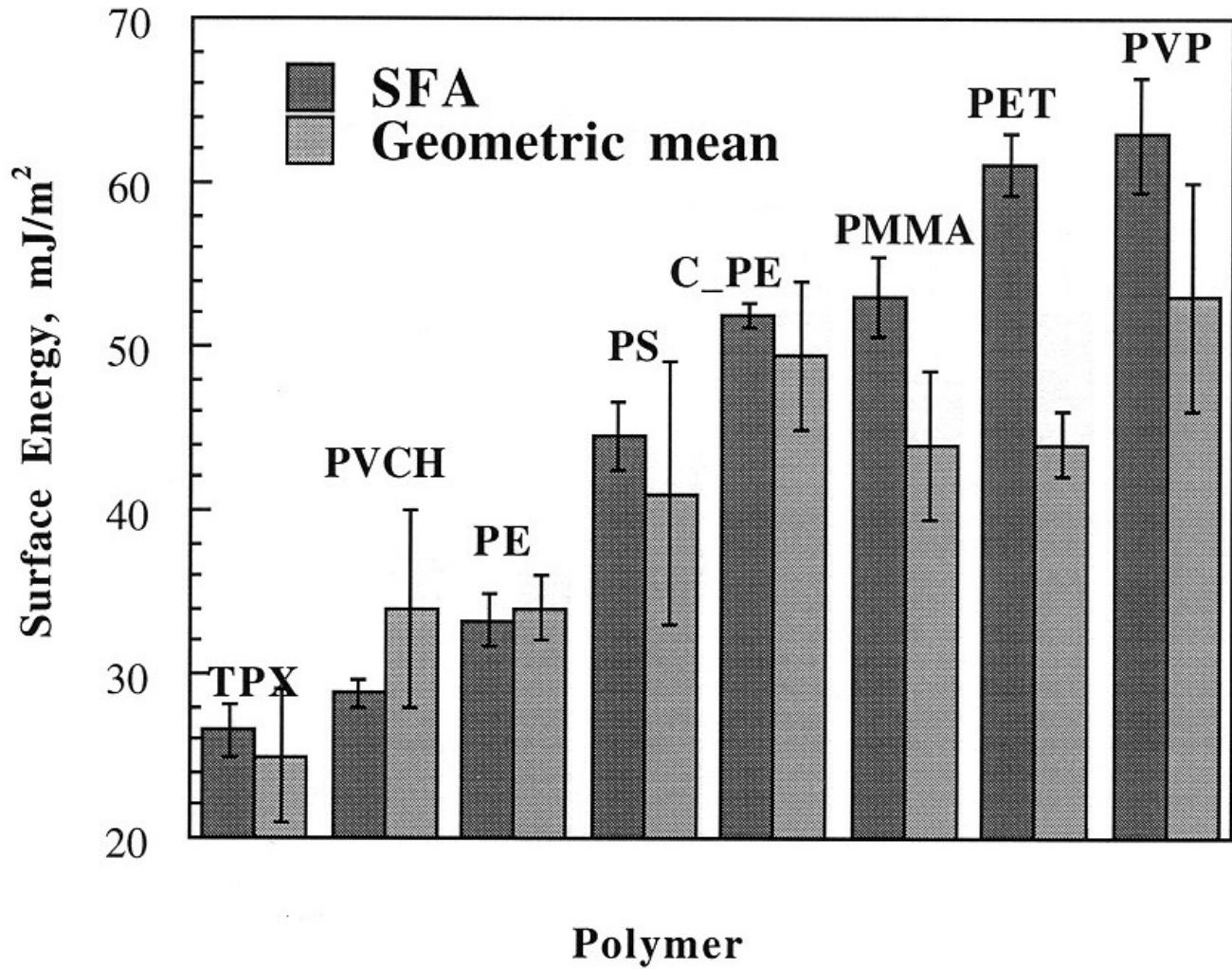
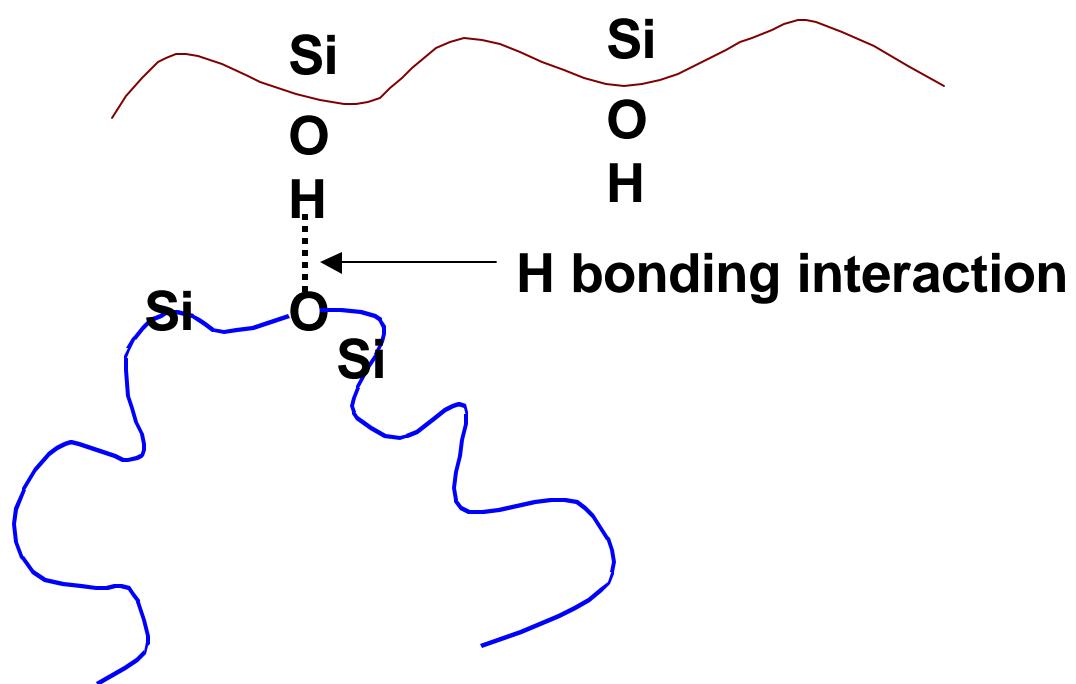
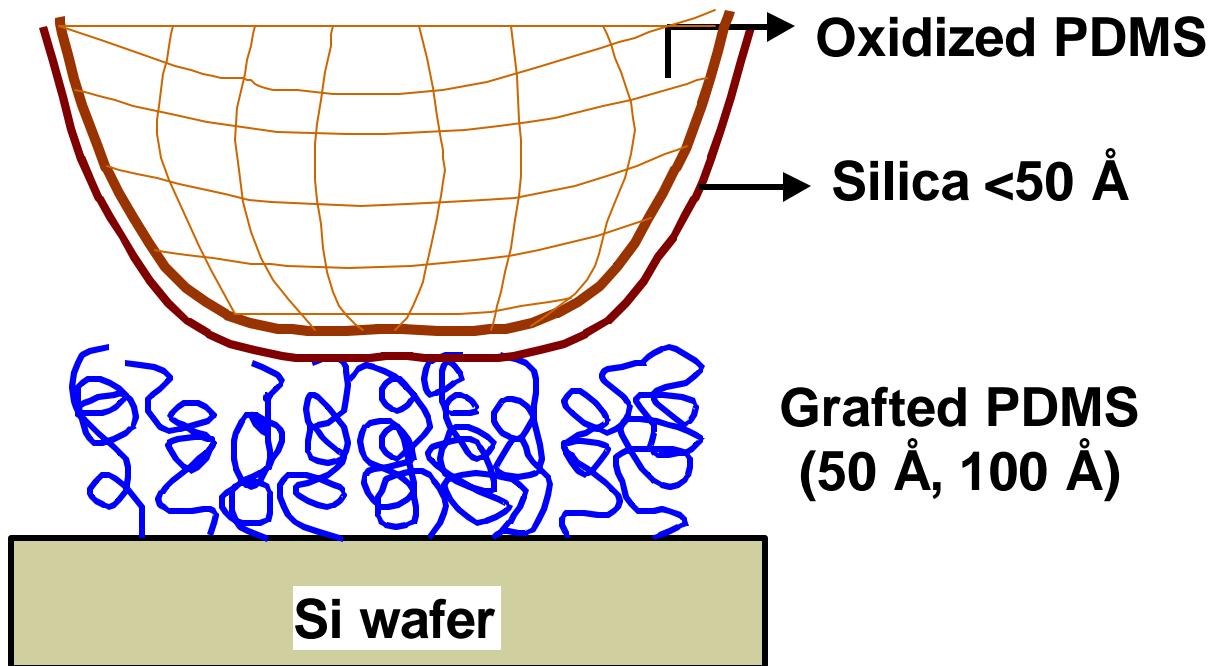


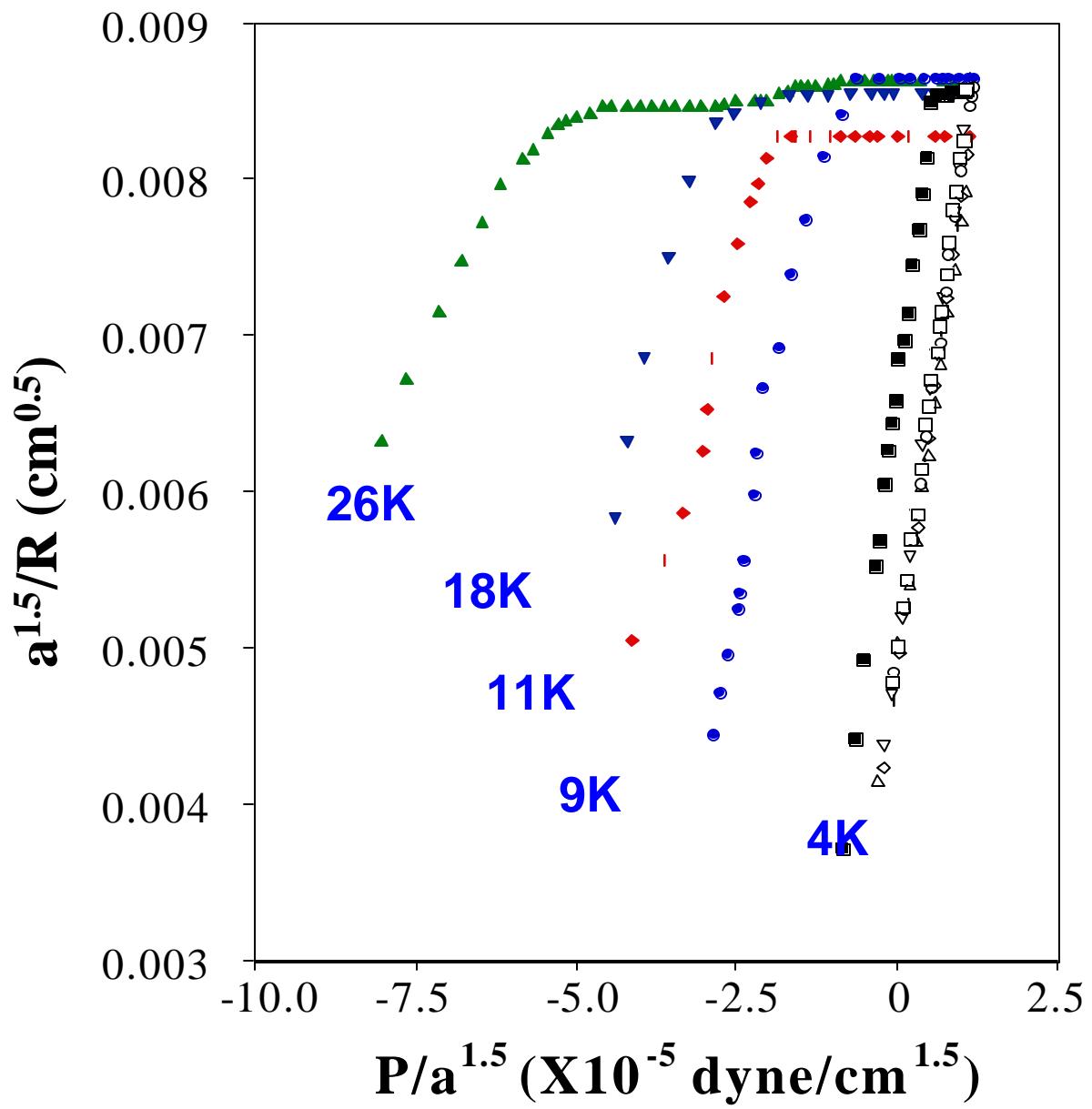
Figure 5. Comparison of the surface energy estimated using the geometric mean approximation and the surface energy measured using the SFA for several polymers.

$\gamma_{geometric}^e$ is estimated by measuring the contact angles of several liquids. γ^d and γ^p are calculated for each pair of liquids, and the mean value is reported. The scatter in the data indicates that the assumptions associated with the geometric mean approximation do not hold in some cases.

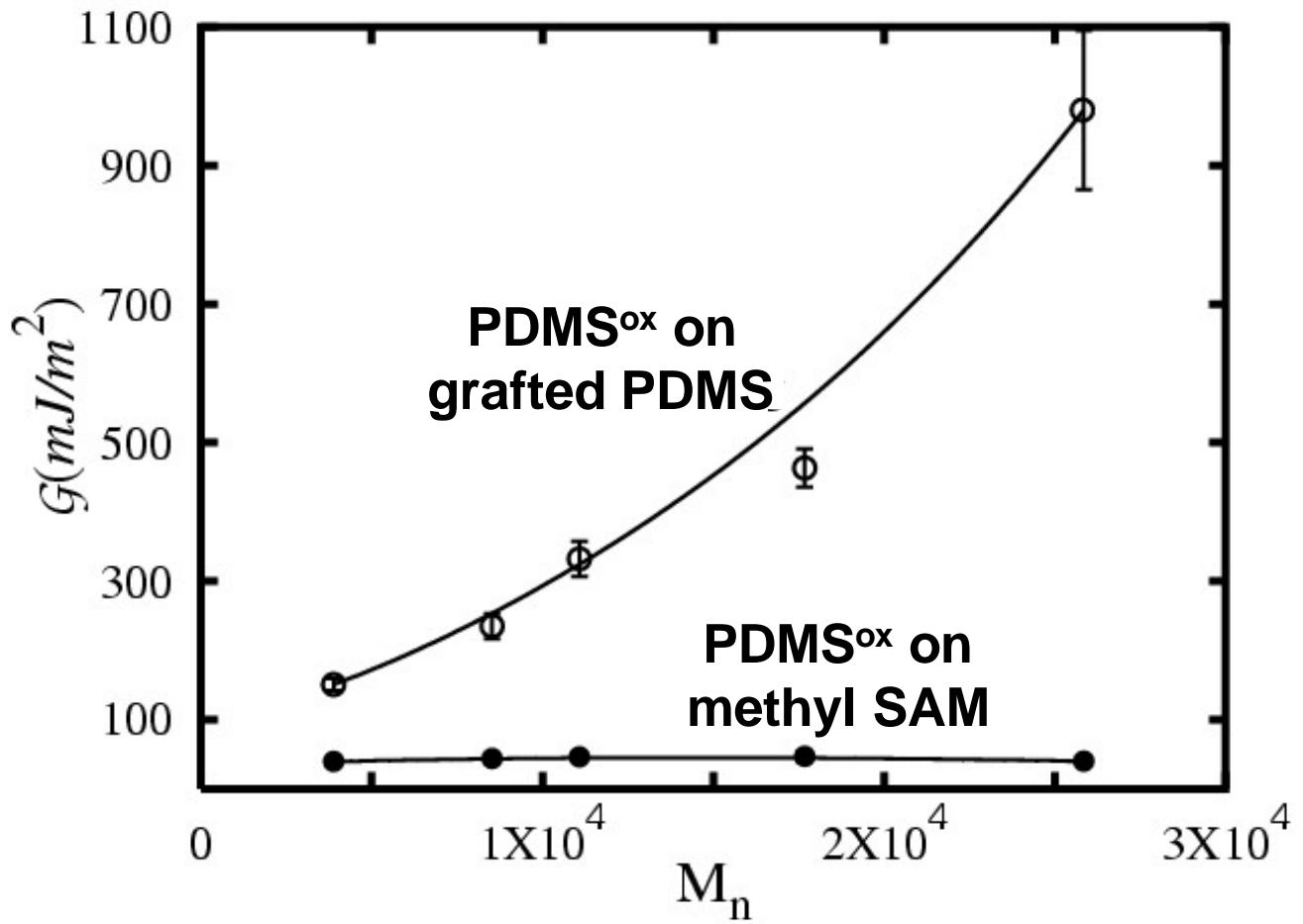
From PhD Thesis
Of V. S. Mangipudi,
Courtesy of
A. V. Pocius, 3

JKR method to study H bonding Interaction



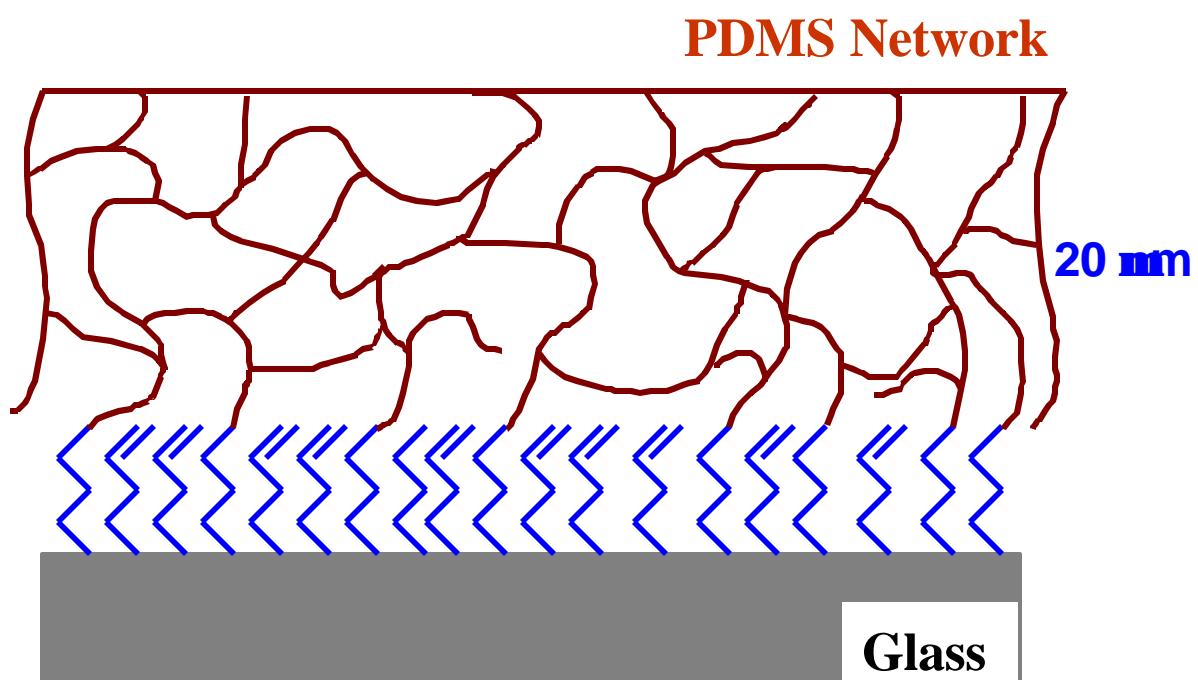


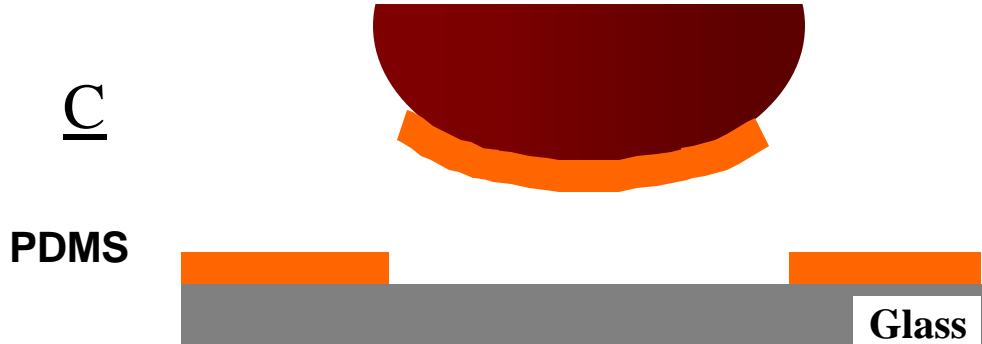
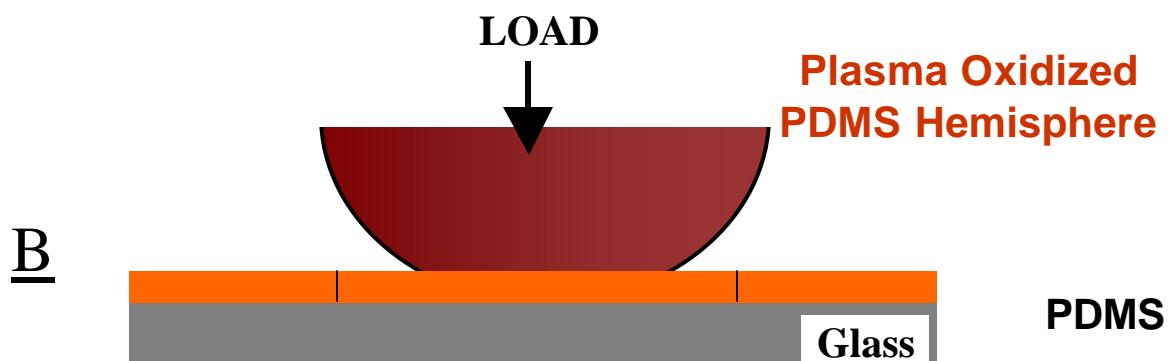
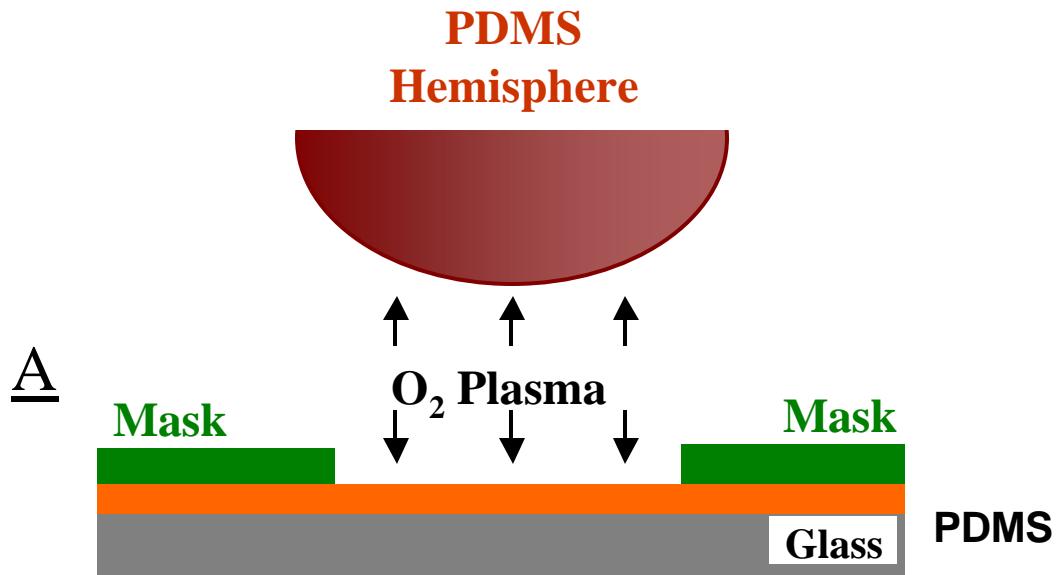
Dependence of fracture energy on molecular weight of polymers



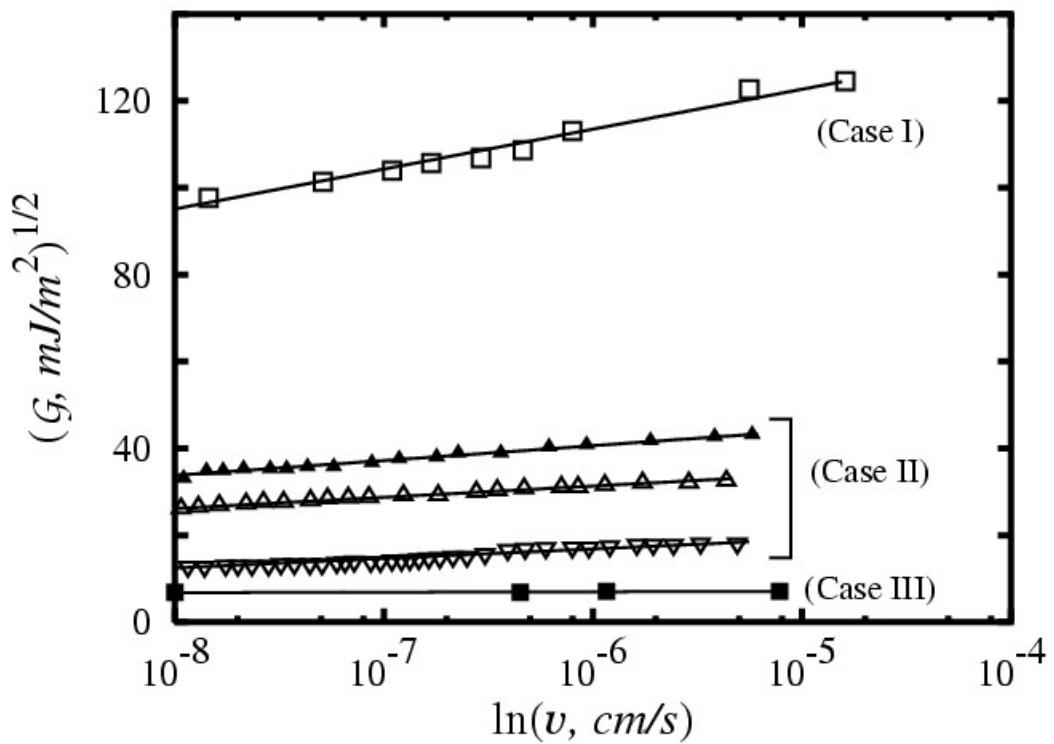
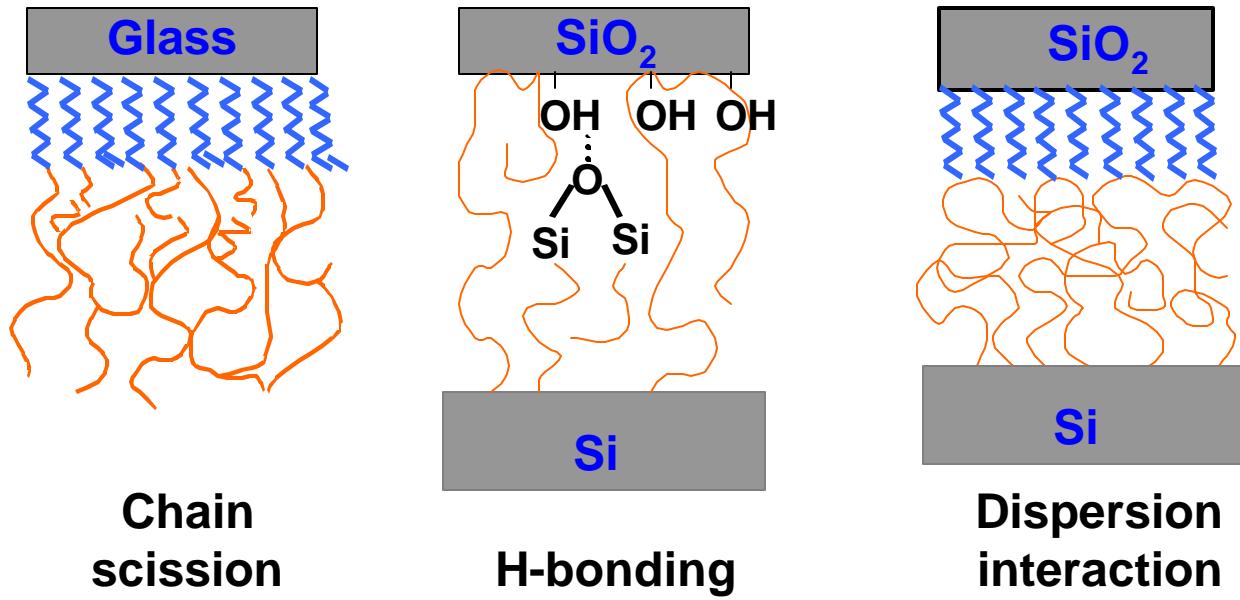
Lake-Thomas Effect
Energy dissipation due to
Orientation and relaxation
of polymer chains

Application of contact mechanics to study strong adhesion (chain scission)

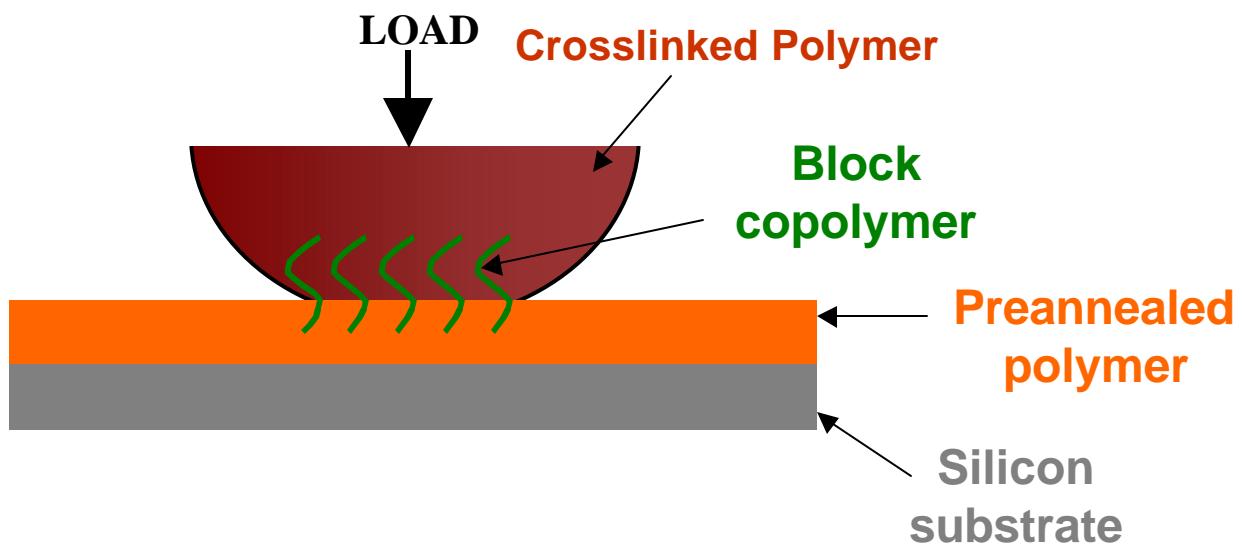
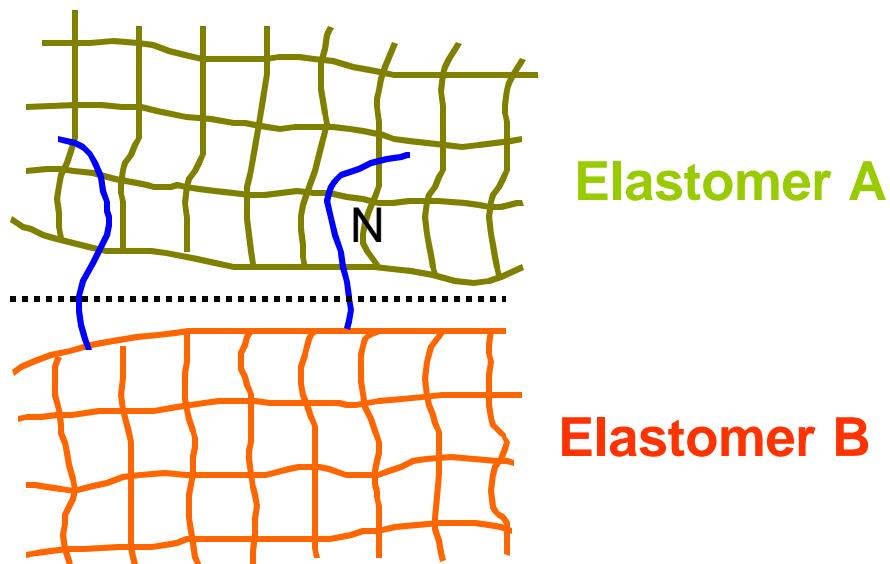




Three model systems for fracture study

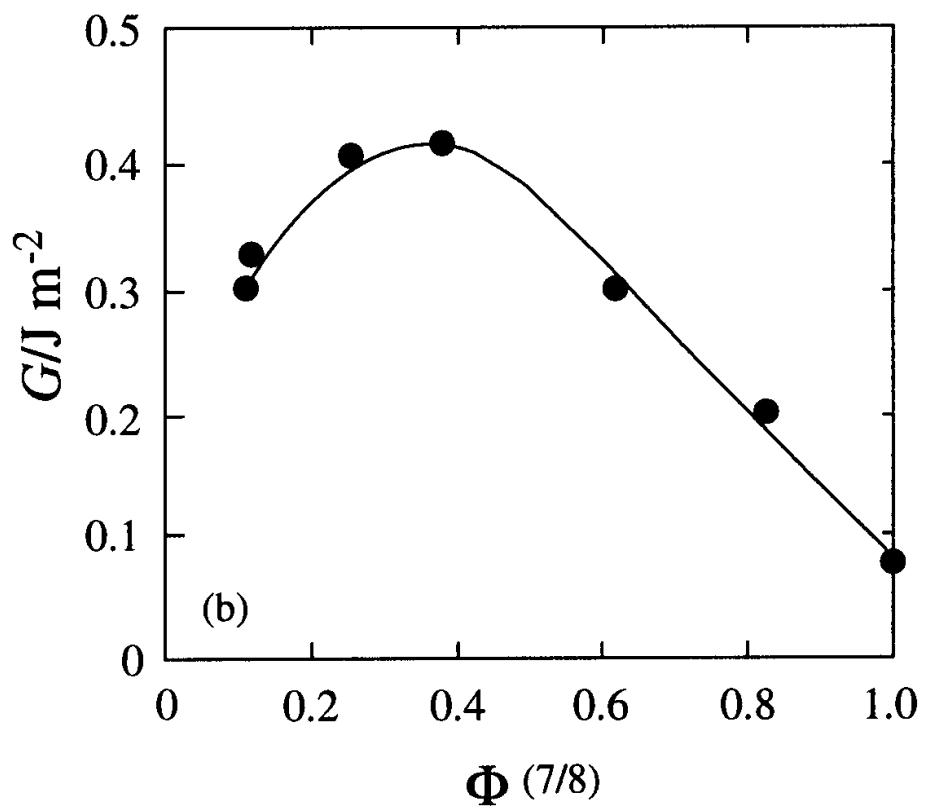
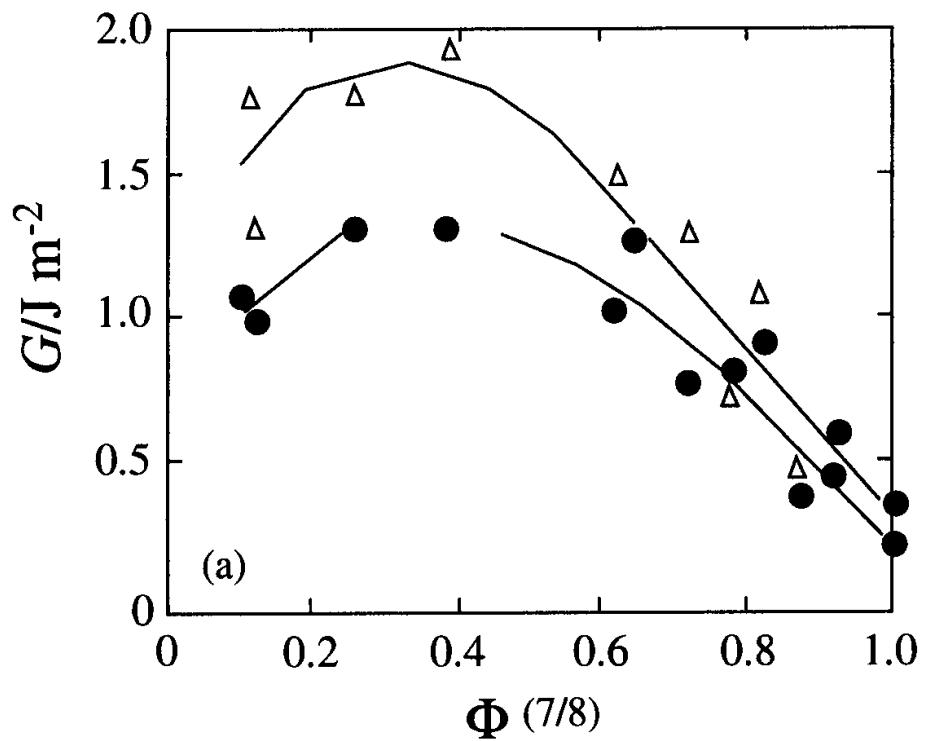


Chain pull-out in fracture



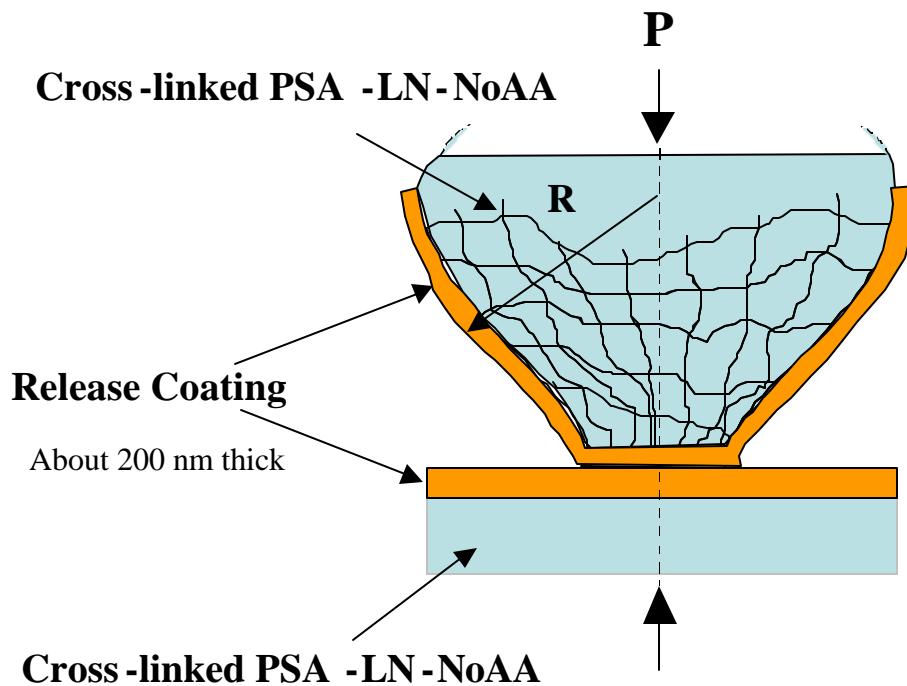
Creton, Brown and Shull, Macromolecules, 27, 3174, 1994

Deruelle, Leger and Tirrell, Macromolecules, 28, 7419, 1995



Bridging the Gap between contact mechanics and peel experiments

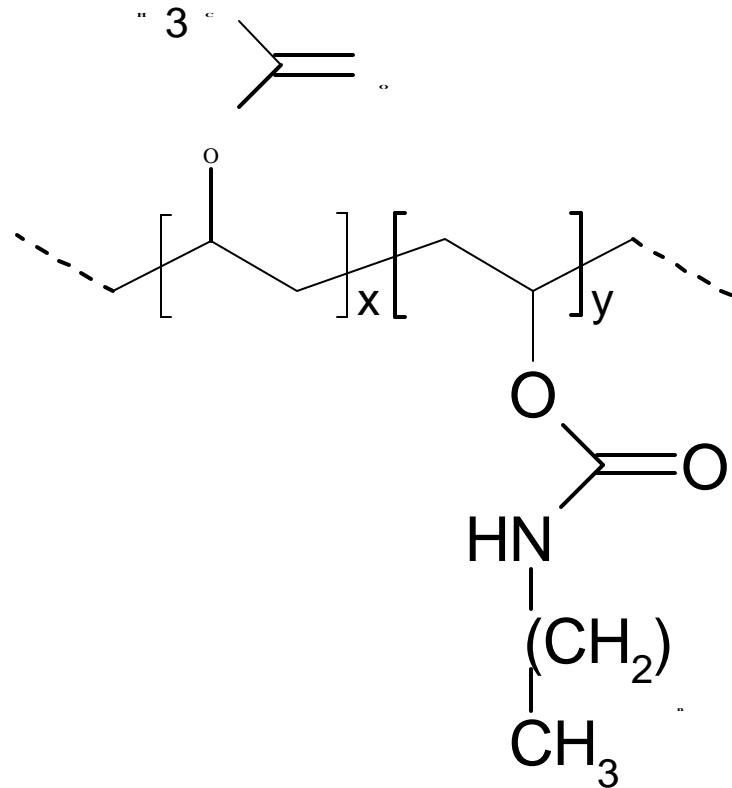
Contact Mechanics Samples



- **Release agents spin coated onto mica**
- **Floated off in water**
- **Picked up on oxygen corona-treated PSA-LN-NoAA cylinders**

Courtesy of A. V. Pocius, 3

Release Agents



poly(vinyl N-alkyl
carbamates)

n=9 => PVNDC

n=17 => PVNODC

Courtesy of A. V. Pocius, 3

Contact Mechanics Samples

- PSA-LN-NoAA = 90% 2-ethyl hexyl acrylate + 10% 1,6-hexanediol diacrylate (sample is almost elastic but with no possibility of silicone contamination)
- PSA-LN-10AA = 80% 2-ethyl hexyl acrylate + 10% acrylic acid + 10% 1,6-hexanediol diacrylate
- PSA-LN-10DMAEA = 80% 2-ethyl hexyl acrylate + 10% dimethylamino ethyl acrylate + 10% 1,6-hexanediol diacrylate

Courtesy of A. V. Pocius, 3

Prepared in capillary tubes (1 mm radius), degassed and initiated with AIBN

Surface Energy (mJ/m²) of PSA-LN's and Release Coatings

Sample	PSA-LN-NoAA	PSA-LN-10AA	PSA-LN-10DMAEA	PVNDC	PVNO DC
Surface Energy	28 <u>±</u> 1	32 <u>±</u> 3* (18)	22	20 <u>±</u> 0.6	20 <u>±</u> 1

Work of Adhesion (mJ/m²) Between PSA-LNs and Release Coatings

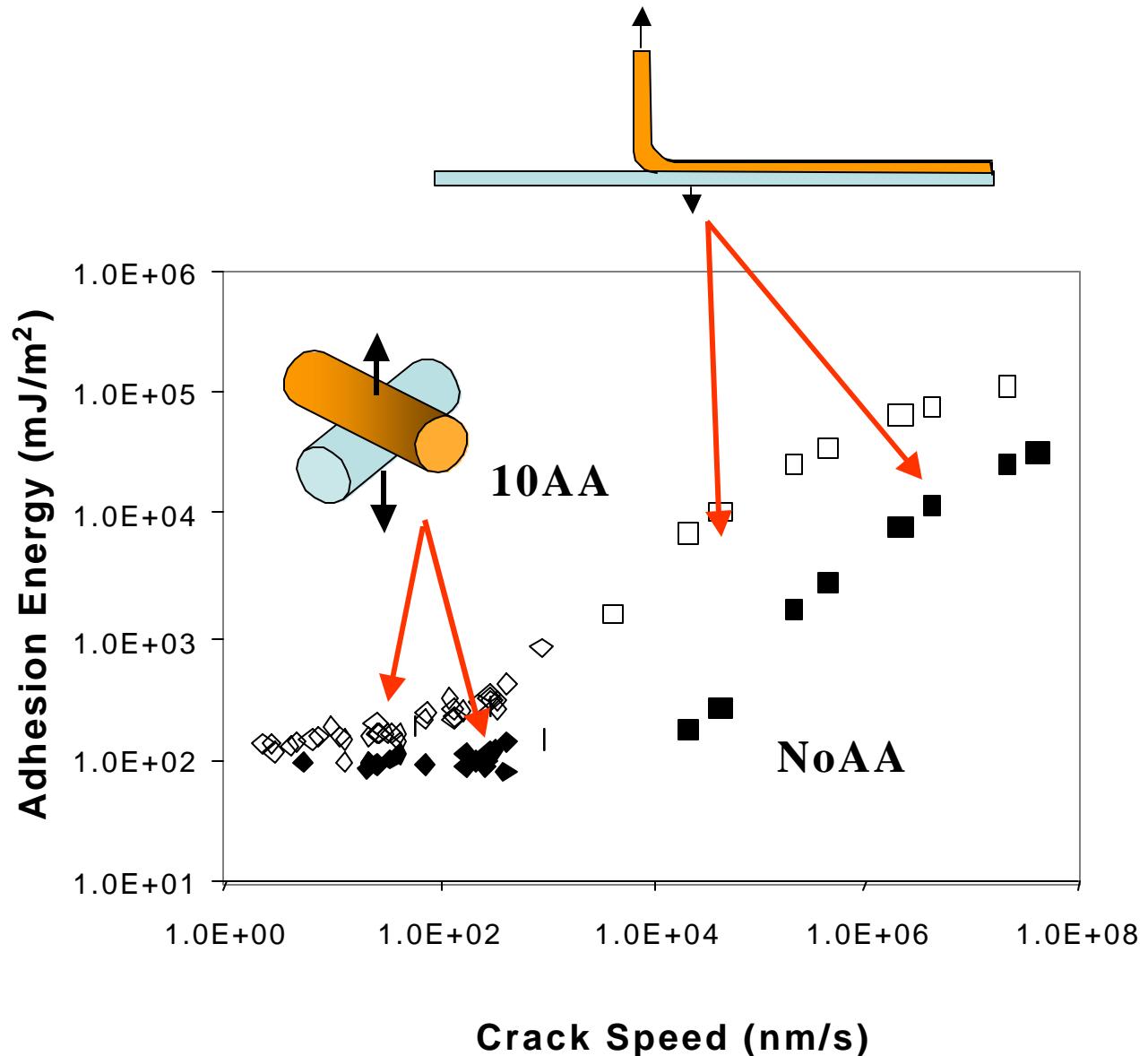
	PSA-LN-NoAA	PSA-LN-10AA
PVNDC	40.2 <u>±</u> 1	27.3 <u>±</u> 1
PVNODC	39.7 <u>±</u> 1	34.2 <u>±</u> 1
PSA-LN-10DMAEA		44.5

Interfacial Energy (mJ/m²) Between PSA-LN's and Release Coatings

	PSA-LN-NoAA	PSA-LN-10AA
PVNDC	7.6 <u>±</u> 1	24.3 <u>±</u> 3
PVNODC	7.6 <u>±</u> 1	17 <u>±</u> 3
PSA-LN-10DMAEA		-12

Courtesy of A. V. Pocius, 3

Adhesion Energy as a Function of Reduced Crack Propagation Rate - Correlation of Peel and Contact Mechanics Measurements



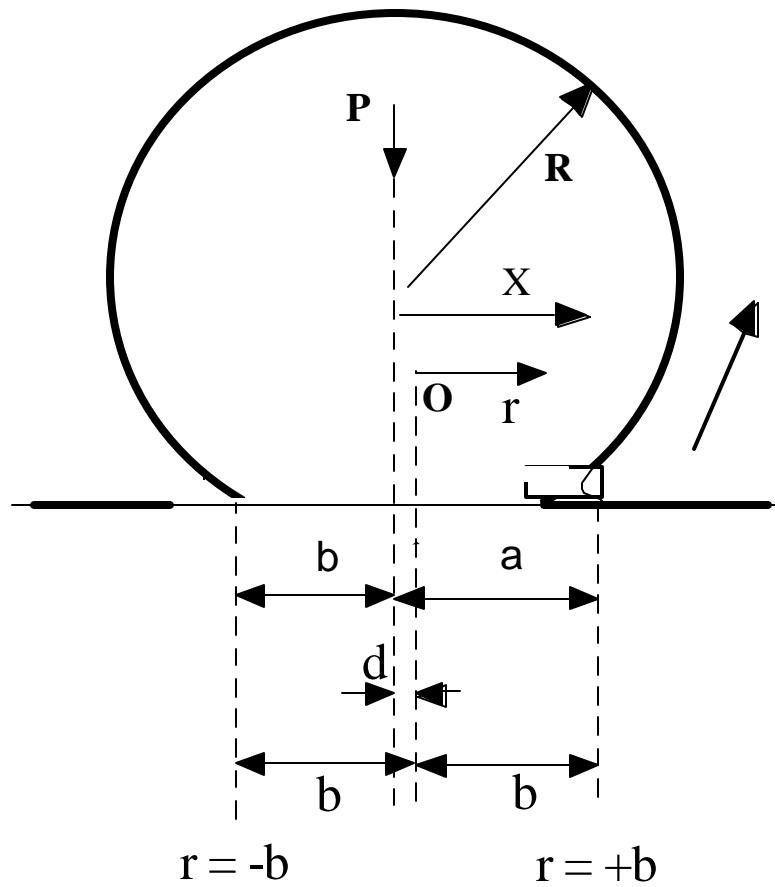
For PVNDC/PSA-LN

Courtesy of A. V. Pocius, 3

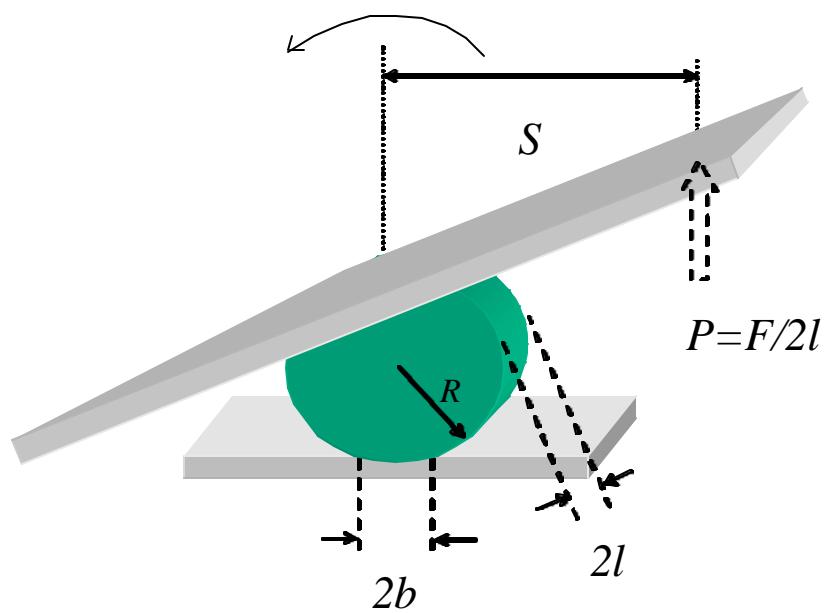
Other Methods

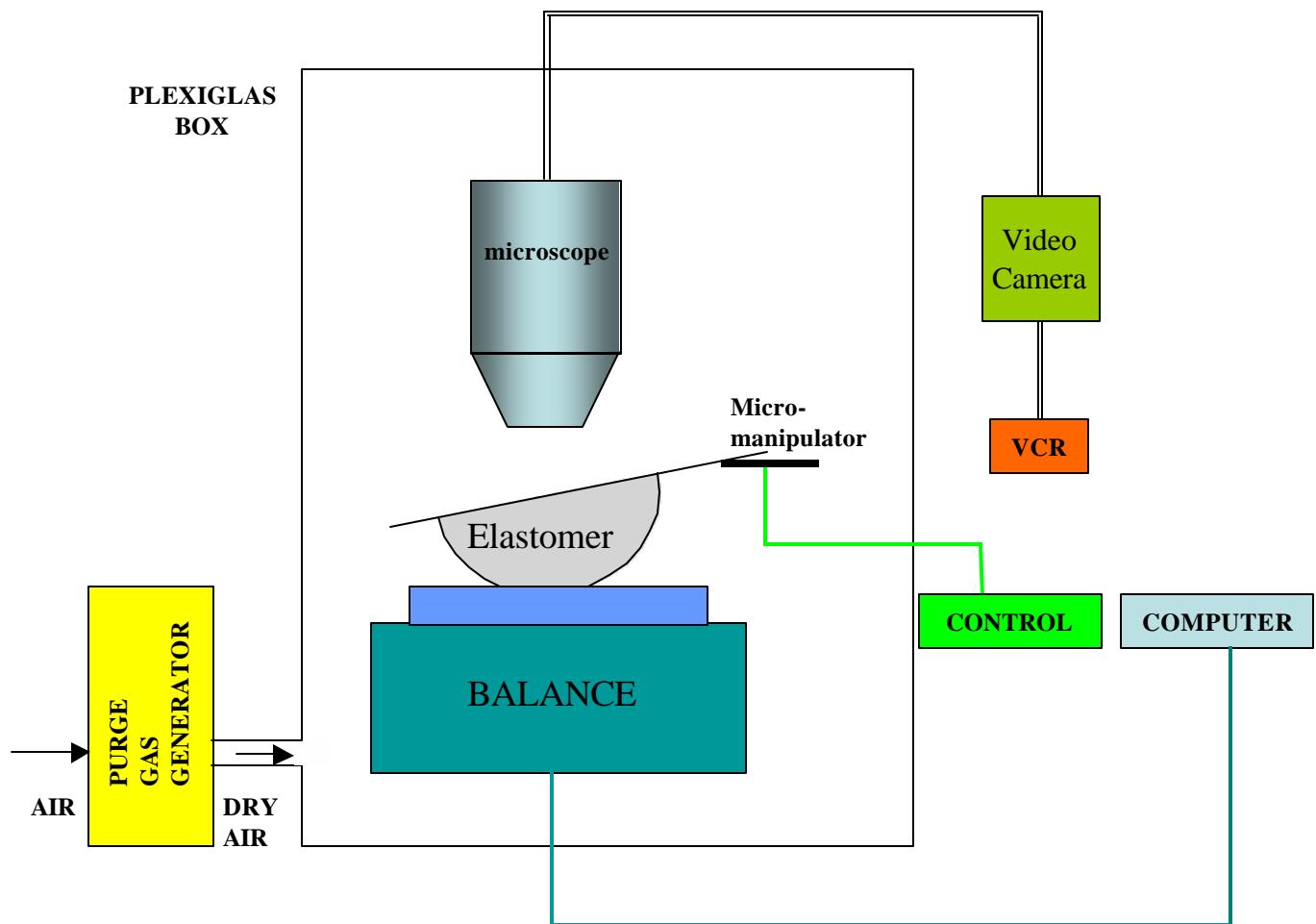
- Rolling Contact Mechanics
- Cantilever Beam
- Peel
- Kendall's Pull-Off Method

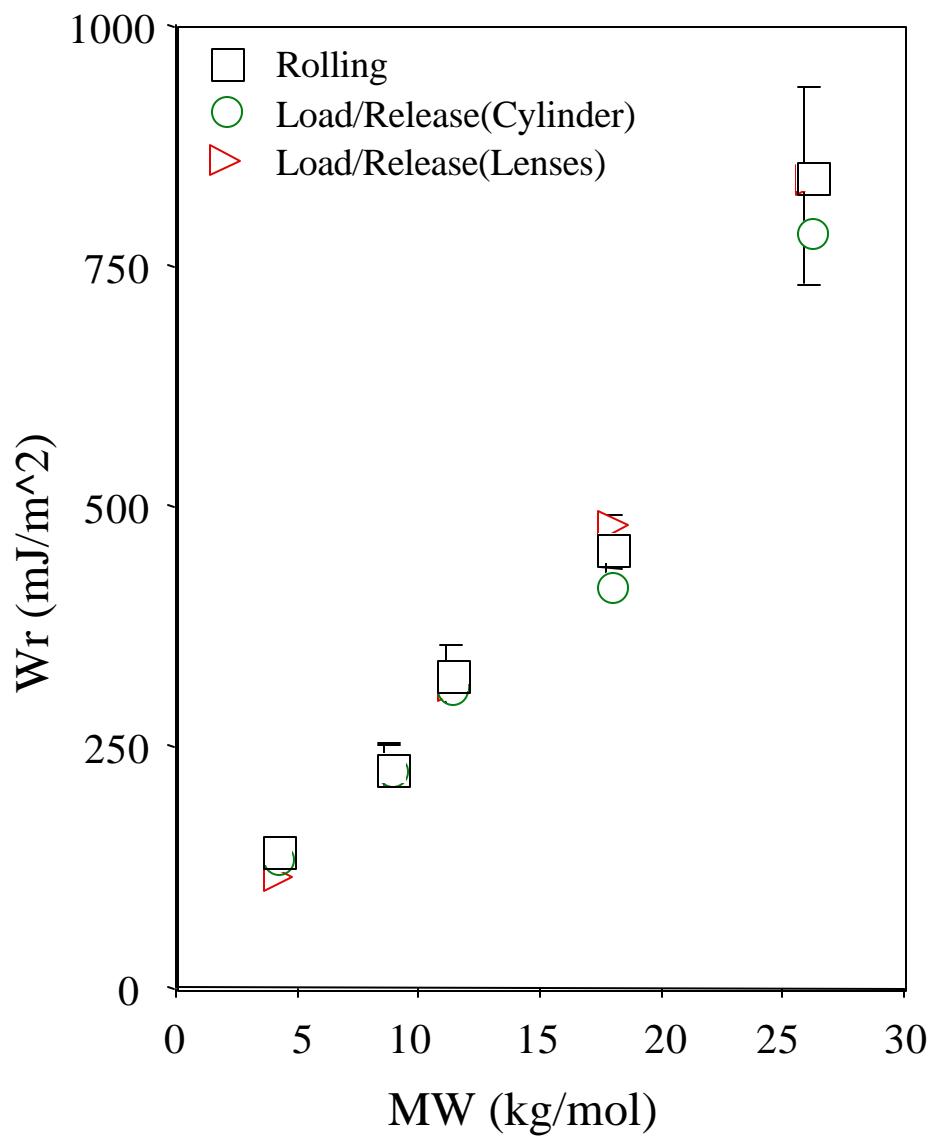
Rolling Contact Mechanics



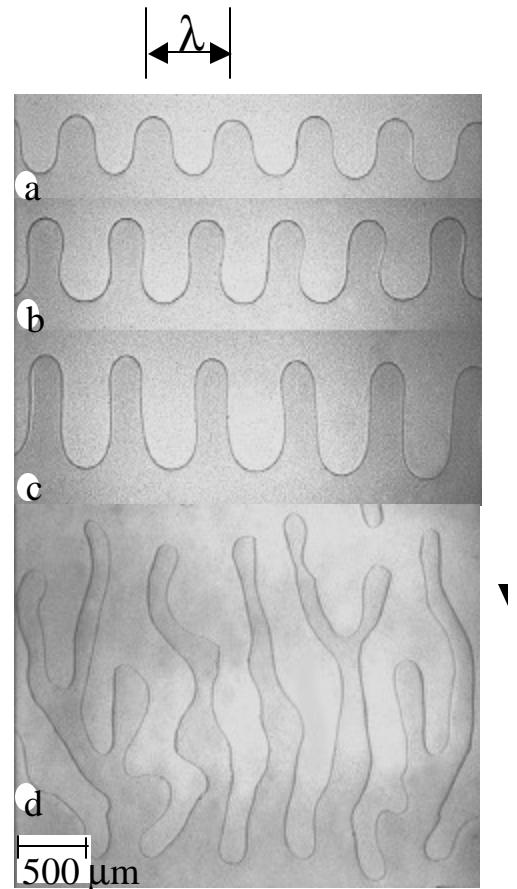
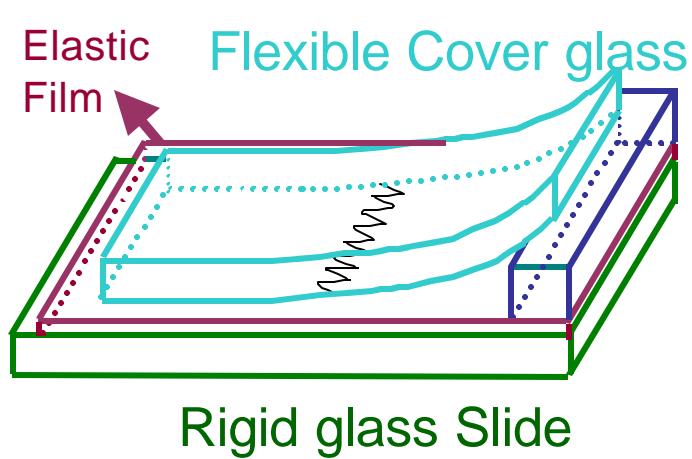
$$t = P \times S$$





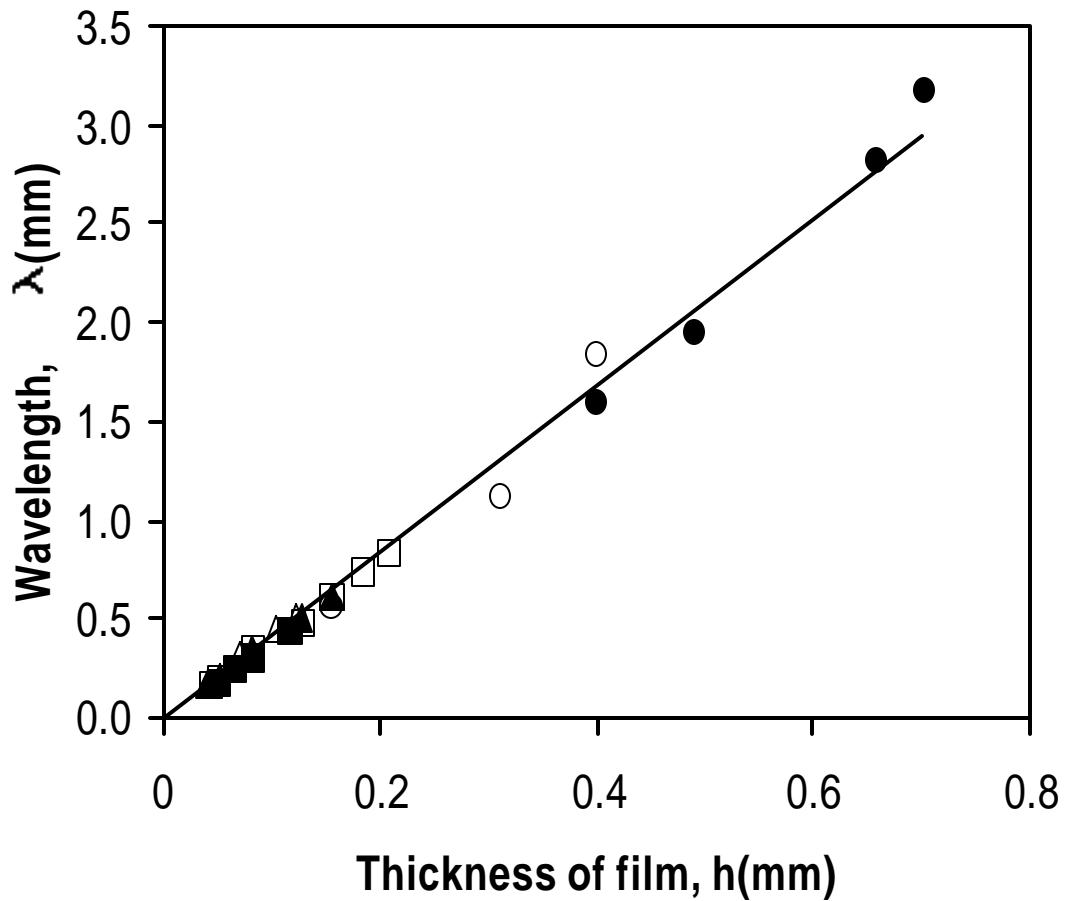


Contact Mechanics using cantilever beam



- Film: $h = 150 \mu\text{m}$, $m = 1.0 \text{ MPa}$

Wavelength :

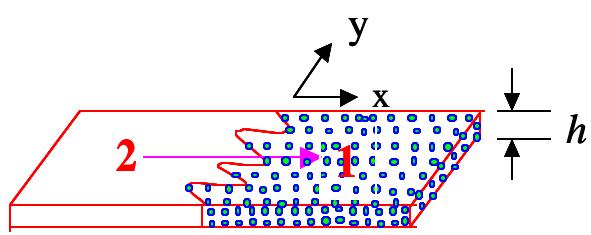


$$\mathbf{I} \sim 4h$$

λ independent of m and D

Interfacial Instability

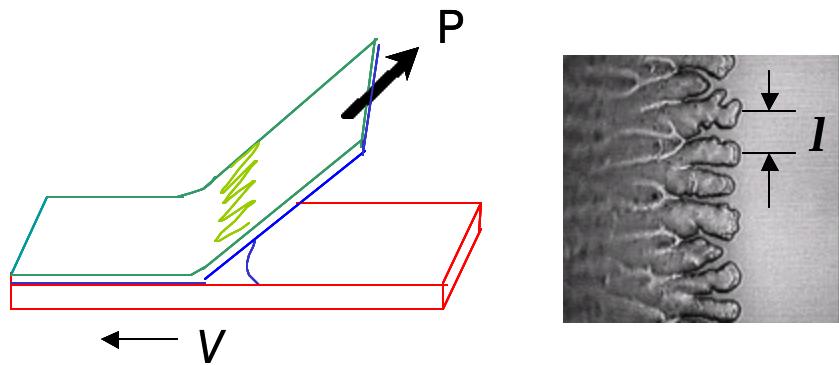
Meniscus Instability in a Helle Shaw cell



Wavelength

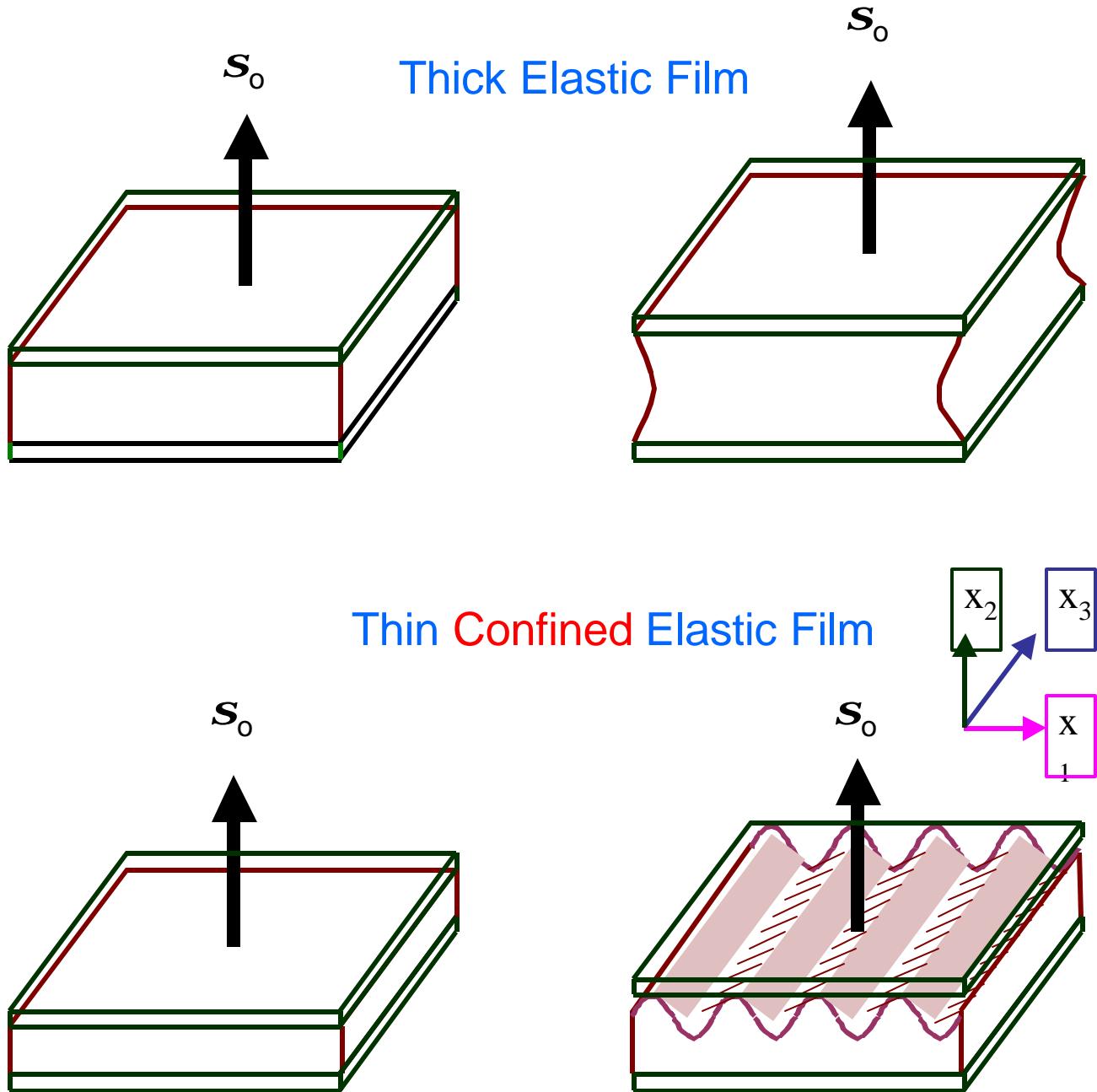
$$l \sim h \sqrt{\frac{g}{hV}}$$

Meniscus Instability in a viscoelastic adhesive :

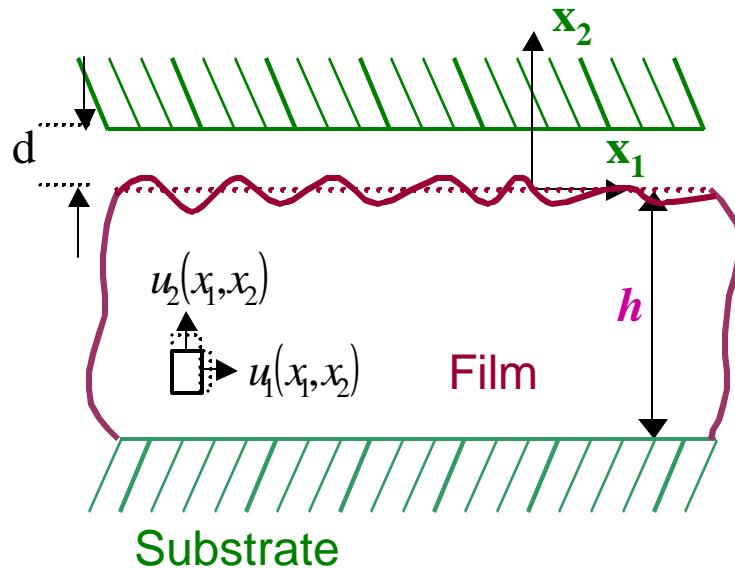


l independent of
 V

Effect of Confinement



Isotropic situation:



Bifurcation
solutions

$$u_1(x_1, x_2) = u_{10}(x_2) \sin(2\pi x_1/\lambda)$$

$$u_2(x_1, x_2) = u_{20}(x_2) \sin(2\pi x_1/\lambda)$$

Solution exist:

van der Waal's spring constant >
elastic spring constant

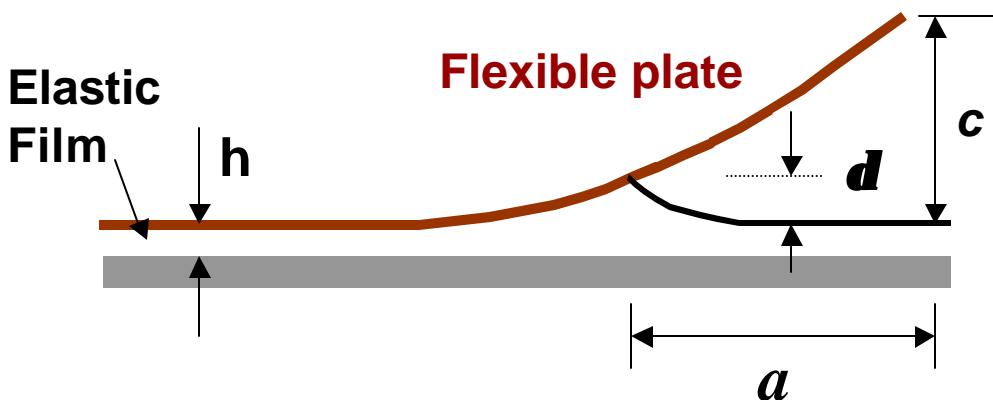
$$I \sim h$$

- ❖ A. Ghatak, M. K. Chaudhury, V. Shenoy and A. Sharma, PRL, Vol 85, 4329-4332 (Nov. 13, 2000).
- ❖ V. Shenoy and A. Sharma, PRL, Vol 86, 119-122 (Jan. 1, 2001).

Derivation of work of adhesion :

$$W = -\frac{2Dk^4}{3} \left(\frac{c - d(ak + 1)}{\frac{2}{3}(ak)^2 + ak} \right)^2 + 2Dk^4 \frac{c - d(1 + ak)}{\left(\frac{2}{3}(ak)^2 + ak \right)^2} \cdot \left(-d \frac{2}{3}ak + (c - d) \left(\frac{4}{3} + \frac{1}{ak} \right) \right)$$

$$d = c \cdot \frac{6(ak)^2 + 15(ak) + 9}{4(ak)^4 + 18(ak)^3 + 30(ak)^2 + 24(ak) + 9}$$



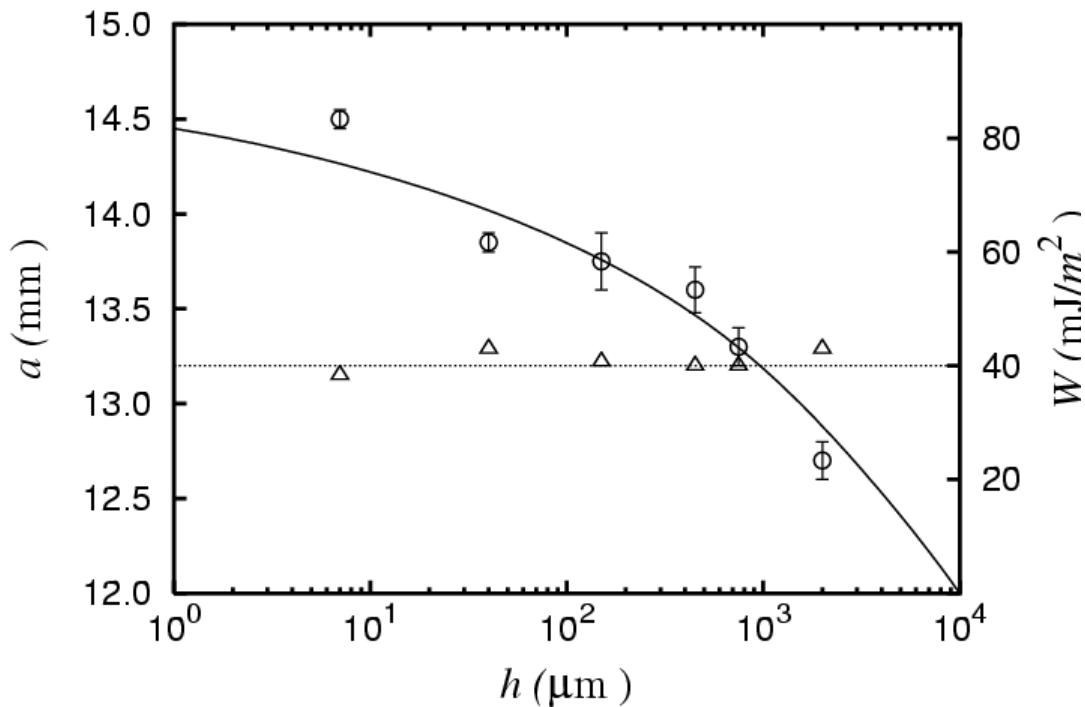
$$k = (E/Dh)^{1/4}$$

D = Rigidity of plate

E = Elastic modulus of film

Cantilever Beam Test

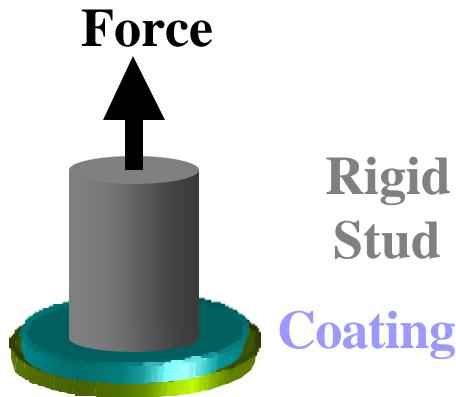
Hydrophobic glass against PDMS film



$$D = 0.02 \text{ Nm}$$

$$E = 3 \text{ MPa}$$

Kendall's equation:



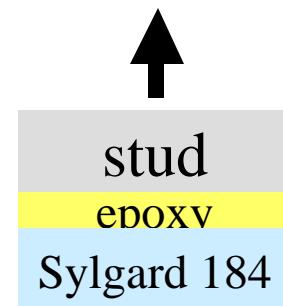
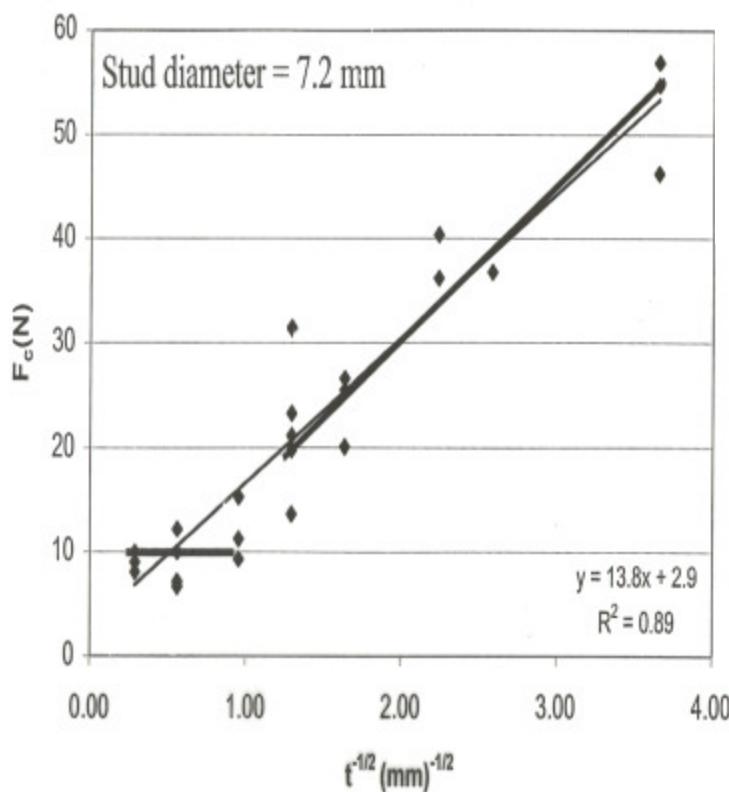
$$\text{Pull-off force} \sim (WE/t)^{1/2}$$

W = Work of adhesion

E = modulus of coating

t = thickness of coating

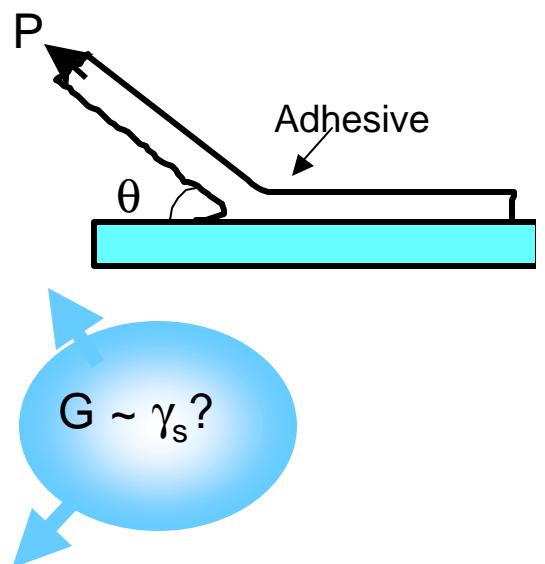
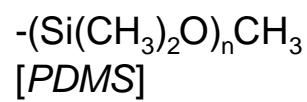
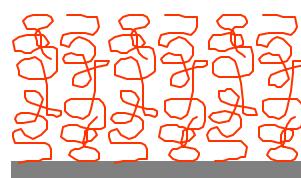
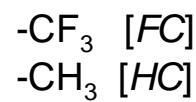
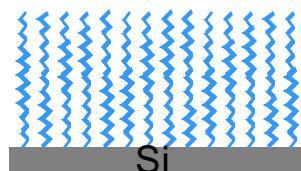
Pull-off Force:



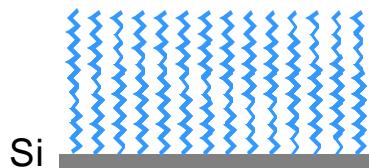
Courtesy:
Patterson and Singer

Some Anomalous Peel Results

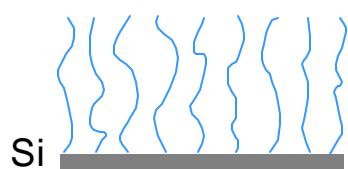
Different Surface Free Energies



Different Phase States

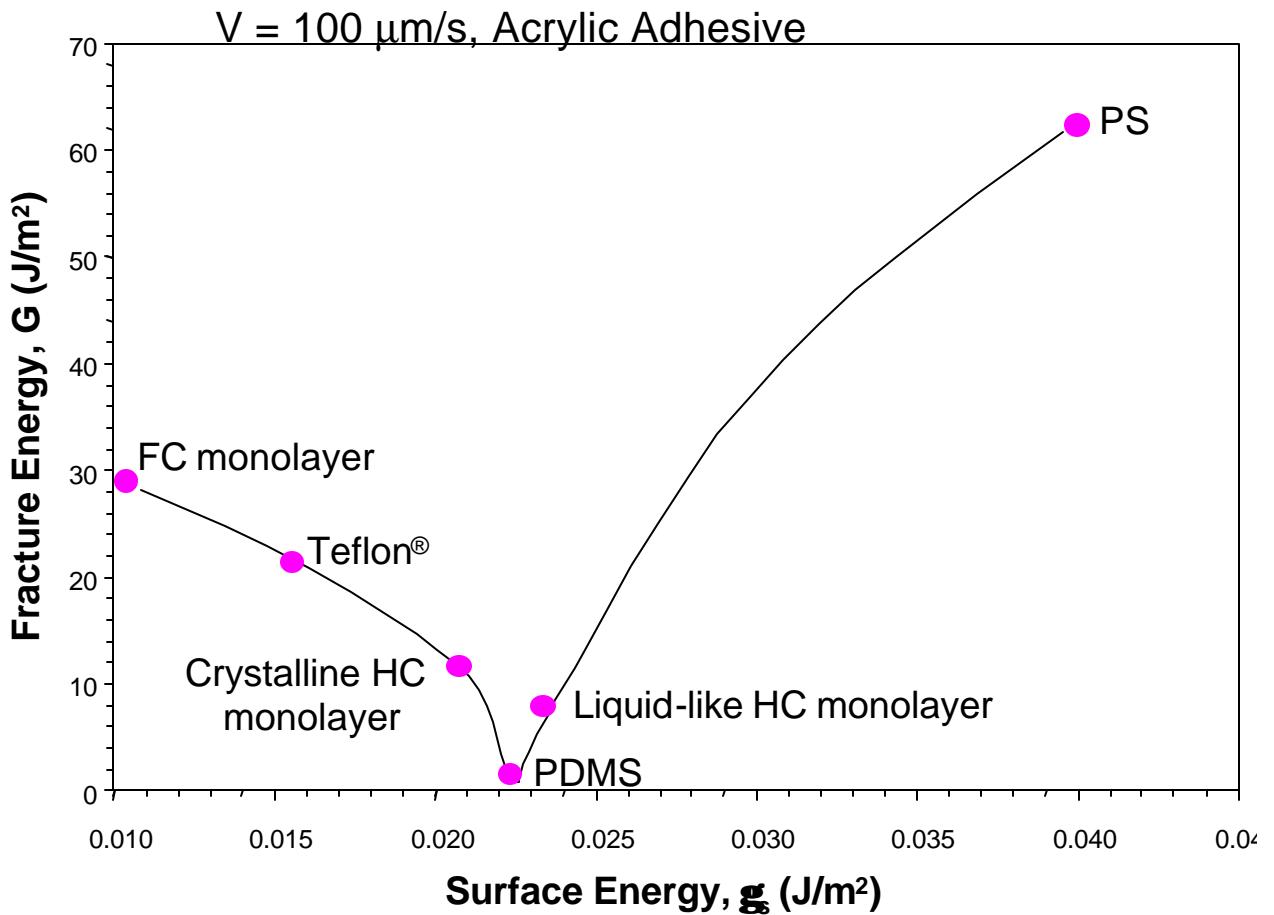


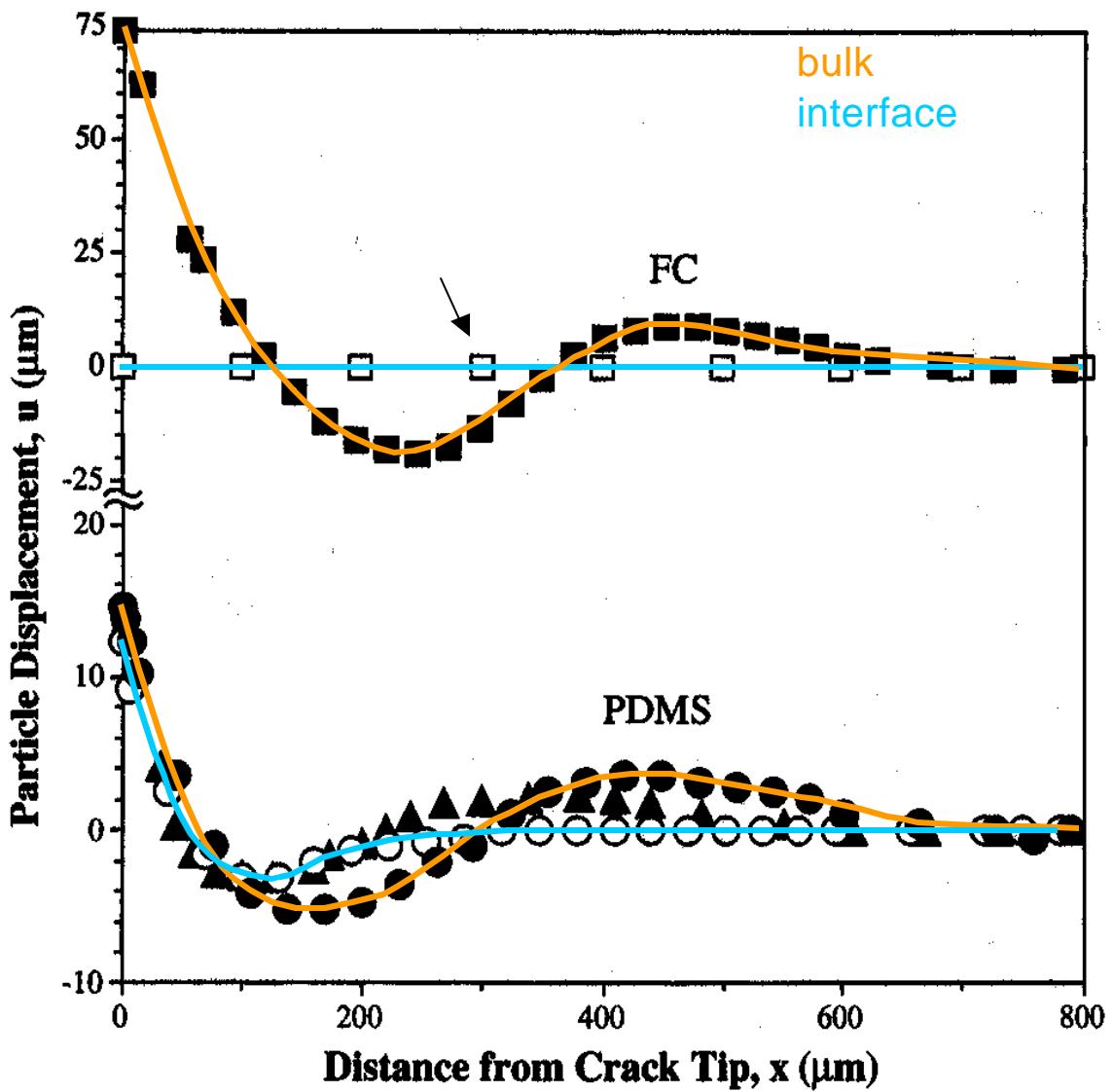
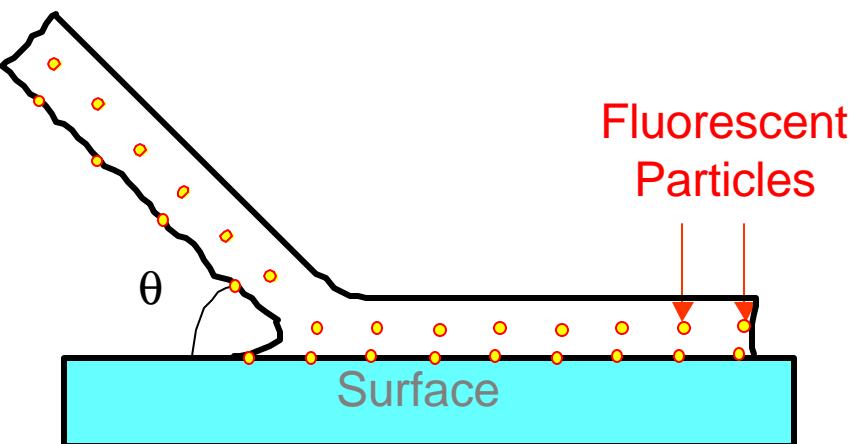
Crystalline SAM



liquid-like SAM

Adhesion of PSA on Low Energy Surfaces





Summary

- JKR method of contact mechanics bridges surface chemistry and mechanics.
- While JKR method has been quite successful, alternate methods could provide complementary information.
- Examination of adhesion induced surface instability could provide valuable information of adhesion and fracture of interfaces.